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(54) Title: NOVEL PHOTOSTABILIZERS, UV ABSORBERS, AND METHODS OF PHOTOSTABILIZING A SUNSCREEN COMPOSITION

(57) Abstract: Polymers and compounds including a diphenylmethylene or a *9H*-fluorene moiety; and sunscreen compositions including a mixture of a photoactive compound and any one of the foregoing derivatives are disclosed herein. Also disclosed are methods for stabilizing a sunscreen composition by the addition of one or more of the foregoing derivatives, methods of filtering out ultra-violet light from a substrate by the use of one or more such derivatives, and methods for terminating a polymerization reaction by the addition of derivatives of diphenylmethylene and/or *9H*-fluorene. Synergistic combinations of the polymer with (1) diesters or polyesters of a naphthalene dicarboxylic acid, or (2) oxybenzone enhance the photostability of sunscreen compositions containing a photodegradable sunscreen active compound, such as avobenzone.

NOVEL PHOTOSTABILIZERS, UV ABSORBERS, AND METHODS OF PHOTOSTABILIZING A SUNSCREEN COMPOSITION

CROSS-REFERENCE TO RELATED APPLICATIONS

This is a continuation-in-part of U.S. Patent Application Serial No. 10/302,423, filed November 22, 2002 which is a continuation-in-part of U.S. Patent Application Serial No. 10/246,434, filed September 17, 2002.

BACKGROUND OF THE INVENTION

Field of the Invention

The invention relates to compounds and methods to increase the photostability of a sunscreen composition. Moreover, the invention relates to photostable sunscreen compositions and a new class of photoactive compounds. More particularly, the invention relates to the use of derivatives of diphenylmethylenemalonic acid and derivatives of fluorene, including polymers terminated with 2-propenoic acid, 2-cyano-3,3-diphenyl- and, specifically, hexanedioic acid/ 2-methyl-2,3-propanediol copolymer terminated with, (2-cyano-3,3-diphenyl-2-propenoate), and referred to herein as Crylene Polymer or CP. Other derivatives include fluorene derivatives of cyano(9H-fluoren-9-ylidene) acetic acid, as well as diesters and polyesters of 9H-fluoren-9-ylidenemalonic acid to photostabilize a sunscreen composition.

Brief Description of Related Technology

It is well known that ultraviolet radiation (light) having a wavelength from about 280 nm or 290 nm to about 320 nm (UV-B) is harmful to human skin, causing burns that are detrimental to the development of a good sun tan. UV-A radiation (about 320 nm to about 400 nm), while producing tanning of the skin, also can cause damage, particularly to very lightly-colored or sensitive skin, leading to reduction of skin elasticity and wrinkles. Therefore, a sunscreen composition for use on human skin preferably includes both a UV-A and a UV-B filter to prevent most of the sunlight within the full range of about 280 nm or 290 nm to about 400 nm from damaging human skin.

Ultraviolet radiation from the sun or artificial sources can also cause harm to coatings containing photoactive substances, such as photoactive pigments and dyes, by

breaking down chemical bonds in the structure of a component such as a polymer, a pigment, or a dye. This photodegradation can lead to color fading, loss of gloss, and loss of physical and protective properties of a coating. Photodegradation can take place in several steps which include one or more components of a coating absorbing UV radiation. The absorbed radiation can excite the absorbing molecules and raise them to a higher energy level, which can be very reactive. If the molecule cannot be relaxed, bond cleavage and the formation of free radicals will occur. These free radicals can attack one or more color molecules and/or a polymer backbone and form more free radicals. UV-A and UV-B filters can also be used to absorb UV radiation to protect a pigmented coating.

The UV-B filters that are most widely used in the U.S. in commercial sunscreen compositions are paramethoxycinnamic acid esters, such as 2-ethylhexyl paramethoxycinnamate, commonly referred to as octyl methoxycinnamate or PARSOL MCX, octyl salicylate, and oxybenzone.

The organic UV-A filters most commonly used in commercial sunscreen compositions are the dibenzoylmethane derivatives, particularly 4-(1,1-dimethylethyl)-4'-methoxydibenzoylmethane (also called avobenzone, sold under the brand name PARSOL 1789). Other dibenzoylmethane derivatives described as UV-A filters are disclosed in U.S. Patent Nos. 4,489,057, 4,387,089 and 4,562,067, the disclosures of which are hereby incorporated herein by reference. It is also well known that the above described UV-A filters, particularly the dibenzoylmethane derivatives, can suffer from rapid photochemical degradation, when used alone or when combined with the above-described most commercially used UV-B filters.

Typically, the above-described UV-B filters are combined with the above described UV-A filters in a solution with other lipophilic or oily ingredients. This solution of oily ingredients, known to formulators of cosmetic products including sunscreens as the "oil phase," is typically, but not necessarily, dispersed with the help of emulsifiers and stabilizers into an aqueous solution composed primarily of water, to make an emulsion which becomes a final cream or lotion form of a sunscreen composition.

The performance of a photoactive compound or a combination of photoactive compounds in a sunscreen composition has been extremely difficult to predict based on the levels of photoactive compounds in the formulation, particularly when the formulation

includes one or more photoactive compounds that suffer from relatively rapid photodegradation, such as avobenzone. Because of this, each formulation has required expensive laboratory testing to determine the UV absorbance, as a function of time (quantity) of exposure of the formulation to UV radiation. Moreover, a particularly difficult problem is presented when one photoactive compound in a sunscreen composition acts to increase the rate of photodegradation of another photoactive compound in the composition. This can be accomplished in a number or ways, including a bimolecular reaction between two photoactive compounds and a lowering of the threshold energy need to raise a photoactive compound to its excited state. For example, when avobenzone is combined with octyl methoxycinnamate a bimolecular pathway leads to the rapid photodegradation of both the dibenzoylmethane derivative and the octyl methoxycinnamate.

Methods and compositions for stabilizing photoactive compounds, such as dibenzoylmethane derivatives with the use of diesters and/or a polyesters of naphthalene dicarboxylic acid are described in U.S. Patent Nos. 5,993,789, and 6,284,916, the disclosures of which are hereby incorporated herein by reference. Other methods of stabilizing a dibenzoylmethane derivative include the addition of an α-cyano-β,β-diphenylacrylate compound to a sunscreen composition including a dibenzoylmethane derivative. *See*, Deflandre et al, U.S. Patent No. 5,576,354 and Gonzenbach et al., U.S. Patent No. 6,033,649.

Brief Description of the Drawings

Figure 1 is a graph of the absorbance of octocrylene (2-ethylhexyl-2-cyano-3,3 diphenylacrylate) and octofluorene (2-ethylhexyl cyano(9H-fluoren-9-ylidene) acetate) from a wavelength of 250 nm to 400 nm, and at a concentration of 10 ppm (parts per million) in cyclohexane.

Figure 2 is a graph of the percent of the original absorbance of sunscreen compositions including 4% by weight of octyl-p-methoxycinnamate and 2% by weight of avobenzone at a wavelength of 370 nm, at various concentrations of octofluorene after the compositions have been exposed to 35 minimal erythemal dose (MED)units, wherein 1 MED is 21 millijoules per square centimeter (mJ/cm2).

Figure 3 is a graph of the percent of the original absorbance of sunscreen compositions including various amounts of octocrylene and octofluorene. The octocrylene and octofluorene were prepared in sunscreen compositions including 7.5% by weight of

octyl-p-methoxycinnamate, 5% by weight of octyl salicylate and 2% by weight of avobenzone, wherein the percent absorbance is measured at a wavelength of 370 nm and at various intervals of exposure to radiation up to and including 35 MED.

Figure 4 is a graph of the percent of the original absorbance of sunscreen compositions including octocrylene and octofluorene at various concentrations in sunscreen compositions including 4% by weight of octyl-p-methoxycinnamate and 2% by weight of avobenzone, wherein the percent absorbance is measured at a wavelength of 310 nm and at various intervals of exposure to radiation, up to and including 35 MED.

Figure 5 is a graph of the percent of the original absorbance of compositions including octocrylene and octofluorene at various concentrations in sunscreen compositions including 4% by weight of octyl-p-methoxycinnamate and 2% by weight of avobenzone, wherein the percent absorbance is measured at a wavelength of 370 nm and at various intervals of exposure to radiation, up to and including 35 MED units.

Figure 6 is a graph of the percent of the original absorbance of the sunscreen compositions listed in Table II, wherein the percent absorbance is measured at a wavelength of 370 nm and at various intervals of exposure to radiation, up to and including 30 MED.

Figure 7 is a graph of the percent of the original absorbance of compositions including octofluorene, octocrylene, diethylhexyl-2,6-naphthalate (DEHN) in a composition including 5% by weight of octyl salicylate and 2% by weight of avobenzone wherein highly polar solvent were included in the oil-phase of the composition to raise the dielectric constant of the oil-phase, and the percent absorbance is measured at a wavelength of 370 nm and at various intervals of exposure to radiation, up to and including 30 MED.

Figure 8 is a graph of the percent of the original absorbance of the sunscreen compositions listed in Table VII, wherein the percent absorbance is measured at a wavelength of 370 nm and at various intervals of exposure to radiation, up to and including 30 MED.

Figure 9 is a graph of the absorbance of the compositions listed in Table VIII from a wavelength of 280 nm to 400 nm and after irradiation at 35 MED.

Figure 10 is a graph of the absorbance of the compositions listed in Table IX from 280 nm to 400 nm after irradiation with 35 MED of Ultraviolet radiation (UVR) from 290 to 400 nm, showing synergy with a combination of CP (bis-2-propenoic acid, 2-cyano-

3,3-diphenyl-terminated adipic acid/methylpropanediol copolymer) and DEHN in stabilizing a dibenzoylmethane derivative, such as avobenzene.

Figure 11 is a graph of the absorbance of the compositions listed in Table IX from 290 nm to 400 nm after irradiation with 120 J/cm^2 of Ultraviolet radiation from 320 to 400 nm, showing synergy with a combination of CP (bis-2-propenoic acid, 2-cyano-3,3-diphenyl-terminated adipic acid/methylpropanediol copolymer) and DEHN in stabilizing a dibenzoylmethane derivative, such as avobenzene.

Figure 12 is a graph of the absorbance of the compositions listed in Table X from 280 nm to 400 nm after irradiation with 35 MED of Ultraviolet radiation from 290 to 400 nm, showing synergy with a combination of CP (bis-2-propenoic acid, 2-cyano-3,3-diphenyl- terminated adipic acid/methylpropanediol copolymer) and oxybenzone in stabilizing a dibenzoylmethane derivative, such as avobenzene.

Figure 13 is a graph of the absorbance of the compositions listed in Table X from 280 nm to 400 nm after irradiation, with 120 J/cm^2 of Ultraviolet radiation from 320 to 400 nm, showing synergy with a combination of CP (bis-2-propenoic acid, 2-cyano-3,3-diphenyl-terminated adipic acid/methylpropanediol copolymer) and oxybenzone in stabilizing a dibenzoylmethane derivative, such as avobenzene.

Summary

One aspect of the invention is a composition including a mixture of a photoactive compound and a compound selected from the group of compounds including derivatives of diphenylmethylenemalonic acid, derivatives of fluorene (*e.g.*, derivatives of cyano(9H-fluoren-9-ylidene) acetic acid, and diesters and polyesters of 9H-fluoren-9-ylidenemalonic acid), and polyesters terminated with a 2-propenoic acid, 2-cyano-3,3-diphenyl- moiety.

Another aspect of the invention includes derivatives of cyano(9H-fluoren-9-ylidene) acetic acid.

Still another aspect of the invention is a diester and/or a polyester of diphenylmethylenemalonic acid.

Still another aspect of the invention are polyesters that are terminated with a 2-propenoic acid, 2-cyano-3,3-diphenyl- moiety and/or a 9*H*-fluorene moiety.

Still another aspect of the invention are polyesters containing a diphenylmethylene moiety.

Still another aspect of the invention is a method of making a polymer by terminating the polymer with compounds including a 2-propenoic acid, 2-cyano-3,3-diphenyl- moiety and/or a 9*H*-fluorene moiety.

Still another aspect of the invention is a method for stabilizing a sunscreen composition including a photoactive compound by the addition of a derivative of 9-methylene-9*H*-fluorene and/or a polyester terminated with a 2-propenoic acid, 2-cyano-3,3-diphenyl- moiety.

Still another aspect of the invention is a method for stabilizing a sunscreen composition including a photoactive compound by the addition of a diester or a polyester of diphenylmethylenemalonic acid.

Another aspect of the invention is a method of filtering out ultra-violet light by the use of a derivative of 9-methylene-9*H*-fluorene and/or a polyester terminated with a 2-propenoic acid, 2-cyano-3,3-diphenyl moiety.

Still another aspect of the present invention is to provide a sunscreen composition containing a combination of an adipic acid/methylpropanediol/2-propenoic acid, 2-cyano-3,3-diphenyl-copolymer or derivative thereof (CP), and a diester or polyester of naphthalene dicarboxylic acid that synergistically photostabilize sunscreen active compounds that are subject to UV-A and/or UV-B photodegradation, particularly a dibenzoylmethane derivative, such as avobenzone.

Still another aspect of the present invention is to provide a sunscreen composition containing a combination of an adipic acid/methylpropanediol/2-propenoic acid,

2-cyano-3,3-diphenyl-copolymer or derivative thereof (CP), and oxybenzone that synergistically photostabilize sunscreen active compounds that are subject to UV-A and/or UV-B photodegradation, particularly a dibenzoylmethane derivative, such as avobenzone.

Detailed Description of the Preferred Embodiments

Sunscreen compositions containing one or more of a photoactive compound, such as a dibenzoylmethane derivative UV-A filter compound, and a derivative of 9-methylene-9*H*-fluorene and/or diesters of diphenylmethylene malonic acid are described herein. One aspect of the sunscreen compositions described herein are methods of photostabilizing a sunscreen composition including a dibenzoylmethane derivative, such as 4-(1,1-dimethylethyl)-4'-methoxydibenzoylmethane (PARSOL® 1789), wherein one or more photoactive compounds present in a sunscreen composition (*e.g.*, avobenzone) are made more photostable by the addition of a derivative of diphenylmethylenemalonic acid and/or a derivative of fluorene, including a derivative of cyano(9H-fluoren-9-ylidene) acetic acid and diesters and/or polyesters of 9H-fluoren-9-ylidenemalonic acid and/or a polyester terminated with a 2-propenoic acid, 2-cyano-3,3-diphenyl- moiety. Also disclosed herein are methods for filtering out ultra-violet light from human skin including the step of applying a derivative of cyano(9H-fluoren-9-ylidene) acetic acid and/or a polyester terminated with a 2-propenoic acid, 2-cyano-3,3-diphenyl- moiety to the skin.

A photoactive compound can be considered stable when, for example, after 30 MED irradiation the photoactive compound has retained at least about 90% of its original absorbance at a wavelength or a range of wavelengths of interest (*e.g.*, the wavelength at which or near a photoactive compound has a peak absorbance, such as 350-370 nm for avobenzone). Likewise, a sunscreen composition can include a plurality of photoactive compounds and a sunscreen composition, as a whole, can be considered stable when, for example, after 30 MED irradiation the sunscreen composition has retained at least about 90% of its original absorbance at one or more wavelengths of interest (*e.g.*, at or near the peak absorbance wavelength of the primary photoactive compounds).

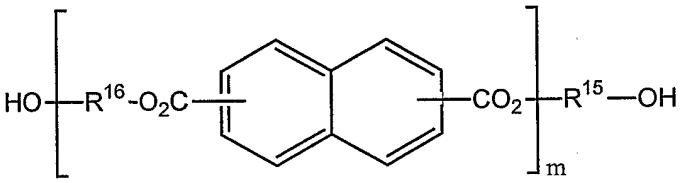
It has surprisingly been found that the addition of one or more of (a) a derivative of diphenylmethylenemalonic acid and/or (b) a derivative of fluorene (including a

derivative of cyano (9H-fluoren-9-ylidene) acetic acid and/or (c) a diester and/or a polyester of 9*H*-fluoren-9-ylidenemalonic acid) and/or (d) a diester or polyester terminated with a 2-propenoic acid, 2-cyano-3,3-diphenyl- moiety to a sunscreen composition including a diester or polyester of naphthalene dicarboxylic acid can significantly increase the photostability of the sunscreen composition and/or photounstable components present therein. Without intending to be limited to any particular mechanism of achieving this increase in stability, it is believed that a diester or polyester of naphthalene dicarboxylic acid stabilizes a dibenzoylmethane derivative by accepting the triplet energy of the dibenzoylmethane derivative once the dibenzoylmethane derivative has reached an excited state as a result of the absorption of ultra-violet light. Once a dibenzoylmethane derivative is excited, it is prone to degrade according to a number of pathways; however, the degradation of the dibenzoylmethane derivative can be substantially reduced or prevented by the use of a diester or polyester of naphthalene dicarboxylic acid to quench (accept) the triplet excited state energy present in an excited dibenzoylmethane molecule. Thus, in one pathway of degradation, a dibenzoylmethane derivative is excited to its triplet state and the excited state triplet energy is released in a bond breaking step, thereby preventing the dibenzoylmethane derivative from further accepting ultra-violet radiation. A diester or polyester of naphthalene dicarboxylic acid may stabilize a dibenzoylmethane derivative by accepting the triplet state (excited state) energy of the excited dibenzoylmethane derivative in such a way as to convert the excited dibenzoylmethane derivative back to a ground state that is capable of reaccepting ultra-violet radiation (energy transfer).

For this process to work continuously, the diester or polyester of naphthalene dicarboxylic acid must transfer or convert the energy that was accepted from the excited dibenzoylmethane derivative. Without intending to be limited to a particular mechanism, it is believed that when a diester or polyester of naphthalene dicarboxylic acid is excited to its triplet state it dissipates the triplet excited state energy through vibrations (*e.g.*, as heat), which in this group of molecules is a relatively slow mode of dissipating energy. It has been found, quite surprisingly, that by the addition of even low levels (*e.g.*, less than 1% by weight) or very low levels (*e.g.*, 0.5% by weight or less) of a derivative of fluorene (*e.g.*, a derivative of cyano(9H-fluoren-9-ylidene) acetic acid and/or a diester and/or a polyester of 9*H*-fluoren-9-ylidenemalonic acid) and/or a polymer terminated with a 2-propenoic acid, 2-

cyano-3,3-diphenyl- moiety such as CP (hexanedioic acid, polymer with 2-methyl-2,3-propanediol, bis(2-cyano-3,3-diphenyl-2-propenoate)), such a compound is able to accept triplet excited state energy from an excited diester or polyester of naphthalene dicarboxylic acid. Thus, according to one possible mechanism, the efficiency of the dissipation of the excited state energy in an excited diester or polyester of naphthalene dicarboxylic acid is greatly improved by a transfer of energy from an excited diester or polyester of naphthalene dicarboxylic acid to a derivative of fluorene (*e.g.*, a derivative of cyano(9H-fluoren-9-ylidene) acetic acid and a diester and/or a polyester of 9*H*-fluoren-9-ylidenemalonic acid).

Thus, preferably, a sunscreen composition disclosed herein includes a diester or polyester of naphthalene dicarboxylic acid selected from the group consisting of compounds of formula (VII), formula (VIII), and combinations thereof:



(VII)

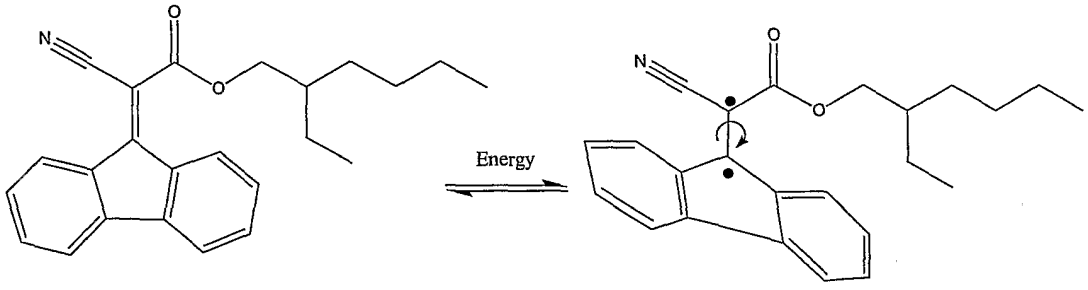
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wherein R^{13} and R^{14} are the same or different and are selected from the group consisting of C_1-C_{22} alkyl groups, diols having the structure HO—R^{15}—OH, and polyglycols having the structure HO—R^{16}—(—O—R^{15}—)$_n$—OH; wherein each R^{15} and R^{16} is the same or different and selected from the group consisting of C_1-C_6 straight or branched chain alkyl groups; and wherein m and n are each in a range of 1 to 100 and p is in a range of 0 to 100. Preferably, a sunscreen composition includes a diester of formula (VIII) wherein R^1 and R^2 are 2-ethylhexane and p is 0.

A sunscreen composition disclosed herein can be combined into a cosmetically acceptable carrier, optionally including emollients, stabilizers, emulsifiers, such as those known in the art, and combinations thereof. These additives can be used in preparing an emulsion from an aqueous system and a mixture of a filter system that includes one or more photoactive compounds and a solvent system that includes one or more organic solvents. When made, preferably the emulsion is an oil-in-water emulsion, wherein the oil phase is primarily formed from a mixture of the filter system and solvent system.

A typical sunscreen composition includes one or more photoactive compounds, wherein a photoactive compound acts to absorb UV radiation and thereby protect the substrate (*e.g.*, human skin) from the harmful effects of UV radiation. The absorption process causes a photoactive compound to reach an excited state, wherein the excited state is characterized by the presence of excited energy (*e.g.*, singlet energy or triplet energy), as compared to the ground state of the photoactive compound. Once a photoactive compound reaches an excited state there exists a number of pathways by which the excited photoactive compound can dissipate its excess energy (*e.g.*, triplet energy), however, many of those pathways adversely affect the ability of the photoactive compound to further absorb UV radiation.

It has surprisingly been found that the addition of one or more of (a) a derivative of diphenylmethylenemalonic acid and/or (b) a derivative of fluorene (including a derivative of cyano(9H-fluoren-9-ylidene) acetic acid and/or (c) a diester and/or polyester of 9*H*-fluoren-9-ylidenemalonic acid) and/or (d) a polyester terminated with a 2-propenoic acid, 2-cyano-3,3-diphenyl- moiety such as CP (hexanedioic acid, polymer with 2-methyl-2,3-propanediol, bis(2-cyano-3,3-diphenyl-2-propenoate)) increases the photostability of a sunscreen composition. Without intending to be limited to any particular mechanism by which a such compounds are able to quench (accept the excited state energy) an excited photoactive compound, it is believed that, for example a 9-methylene-9*H*-fluorene derivative accepts the excited state energy and dissipates the energy kinetically in the form of rapid isomerizations. An example of this process is shown below:



A A*

wherein the 9-methylene-9H-fluorene derivative (2-ethylhexyl cyano(9H-fluoren-9-ylidene) acetate, shown above as A and hereinafter referred to as octofluorene), accepts the triplet excited state energy and forms a diradical (shown above as A^*) at the α and β positions of the

acrylate, which converts the double bond into a single bond and allows for free rotation about the single bond. This rotation occurs rapidly and efficiently to dissipate excited state energy accepted by a derivative of fluorene.

Commonly-assigned U.S. Patent Application Serial Nos. 10/092,131, filed March 5, 2002, and 10/092,132, now U.S. Patent No. 6,485,713, the disclosures of which are hereby incorporated herein by reference, describe compositions and methods for increasing the stability of photoactive compounds in a sunscreen composition, *e.g.*, by the addition of polar solvents to the oil phase of a composition. It has been found, quite surprisingly, that by increasing the polarity of the oil phase of a sunscreen composition including one or more of a derivative of diphenylmethylene and a derivative of fluorene, the stability of the sunscreen composition is increased. Now knowing that the polarity of the solution affects the stability, one might expect that the more polar the solution is, the greater the stability it will impart to the photoactive compound. In contrast, and even more surprisingly, it has been found that as the polarity of a solvent system including a dissolved, rapidly photodegradable compound is increased, the rate of photodecay initially decreases but then increases again as the polarity is further increased. Thus, a photodegradable compound in solution will degrade as a second-order function of the overall polarity of the solution. Currently accepted photochemical theory provides the possibility that the mechanism by which a photodegradable compound is stabilized is the transfer of a photonically-excited electron to a nearby molecule of the same or different species (*see, e.g.*, N.J. Turro, Modern Molecular Photochemistry, Chapter 9, Benjamin/Cummings Publ. Co., Menlo Park, California (1991)), however photochemical theory does not describe the observed phenomena. Though not intending to be bound by such a belief, the observed phenomena are believed to coincide with the electron transfer theory of Professor Rudolph A. Marcus of the California Institute of Technology, for which he received the 1992 Nobel Prize in Chemistry.

The dielectric constant of a solvent system is a preferred measure of polarity of a solvent system, for example because the dielectric constant is a measure of both inherent and inducible dipole moments. Other measures of polarity include, but are not limited to, the induced and/or inherent (permanent) dipole moment (*e.g.*, in Debye units), the Dimroth-Reichardt E_T parameter, and ionizing power. See generally, C. Reichardt, "Solvents and

Solvent Effects in Organic Chemistry" 2nd ed., Chap. 7: Empirical Parameters of Solvent Polarity, VCH Publishers, New York, New York, (1988). Moreover, a more detailed description of these methods of measuring the polarity of the compound or a series of compounds can be found in commonly assigned U.S. Patent Application Serial Nos. 10/092,131 and 10/092,132.

Mathematically, photodegradation can be described by an exponential function. Thus, Q(a), the absorbance after a radiation dose (*i.e.*, exposure to a quantity of radiation), can be described by the general equation (i),

$$Q(a) = Ae^{-kr} \qquad \text{(i)}$$

wherein A is the original (pre-exposure) absorbance, e is the natural logarithm base, k is the rate constant of the photodecay, and r is the cumulative dose (*e.g.*, in MED units). Because the absorbance decreases as the cumulative dose increases (photodecay), the overall term $-k$ will be negative, and the greater the value of $-k$ (*i.e.*, closer to zero) and, thus, the lower the rate constant of photodecay, the lower is the rate of photodecay. For example, when Q(a) is plotted on a log scale versus r on a linear scale, the function forms a straight line with a slope equal to $-k$.

Furthermore, it has been found that, for a set of photoactive compounds that includes a photodegradable compound (*e.g.* avobenzone), the rate constant of photodecay of the set of photoactive compounds can be described as a second-order function of the polarity, preferably the dielectric constant (*i.e.*, relative permittivity) of the filter set dissolved in the solvent system. Thus, for example, the rate constant of photodecay of a filter set that include one or more of a photoactive compound, can be described by the general equation (ii),

$$k = -(x\varepsilon^2 + y\varepsilon + z) \qquad \text{(ii)}$$

wherein x, y, and z can be empirically determined. The dielectric constant at the theoretical minimum rate constant of photodecay -k min described by formula (iii),

$$\varepsilon_{k\,min} = \frac{-y}{2x} \qquad \text{(iii)}$$

wherein x and y are defined as above.

The phenomena described above, coupled with the knowledge that, heretofore, sunscreen compositions have been formulated without specific regard to the relationship between polarity and photostability and, in newly-discovered fact, have had non-optimal polarities, forms the basis for at least one aspect of the compositions and methods described herein.

In a sunscreen disclosed herein, preferably, one or more of a highly polar solvent is present in the oil-phase of the composition. Preferably, a sufficient amount of a polar solvent is present in a sunscreen composition to raise the dielectric constant of the oil-phase of the composition to a dielectric constant of at least about 7, preferably at least about 8.

A photoactive compound is one that responds to light photoelectrically. In the compositions disclosed herein, a photoactive compound is one that responds to UV radiation photoelectrically. For example, photoactive compounds that respond to UV radiation photoelectrically by rapid photodegradation can benefit highly from the compositions and methods disclosed herein, even though the benefits of the compositions and methods disclosed herein are not limited to such compounds. Photostability is a potential problem with all UV filters because they are deliberately selected as UV-absorbing molecules. In other applications, a photoactive compound may be a pigment or a dye (*e.g.*, a hydrophobic dye).

UV filters include compounds selected from the following categories (with specific examples) including: p-aminobenzoic acid, its salts and its derivatives (ethyl, isobutyl, glyceryl esters; p-dimethylaminobenzoic acid); anthranilates (o-aminobenzoates; methyl, menthyl, phenyl, benzyl, phenylethyl, linalyl, terpinyl, and cyclohexenyl esters); salicylates (octyl, amyl, phenyl, benzyl, menthyl (homosalate), glyceryl, and dipropyleneglycol esters); cinnamic acid derivatives (menthyl and benzyl esters, alpha-phenyl cinnamonitrile; butyl cinnamoyl pyruvate); dihydroxycinnamic acid derivatives (umbelliferone, methylumbelliferone, methylaceto-umbelliferone); camphor derivatives (3-benzylidene, 4-methylbenzylidene, polyacrylamidomethyl benzylidene, benzalkonium

methosulfate, benzylidene camphor sulfonic acid, and terephthalylidene dicamphor sulfonic acid); trihydroxycinnamic acid derivatives (esculetin, methylesculetin, daphnetin, and the glucosides, esculin and daphnin); hydrocarbons (diphenylbutadiene, stilbene); dibenzalacetone; benzalacetophenone; naphtholsulfonates (sodium salts of 2-naphthol-3,6-disulfonic and of 2-naphthol-6,8-disulfonic acids); dihydroxy-naphthoic acid and its salts; o- and p-hydroxydiphenyldisulfonates; coumarin derivatives (7-hydroxy, 7-methyl, 3-phenyl); diazoles (2-acetyl-3-bromoindazole, phenyl benzoxazole, methyl naphthoxazole, various aryl benzothiazoles); quinine salts (bisulfate, sulfate, chloride, oleate, and tannate); quinoline derivatives (8-hydroxyquinoline salts, 2-phenylquinoline); hydroxy- or methoxy-substituted benzophenones; uric acid derivatives; vilouric acid derivatives; tannic acid and its derivatives; hydroquinone; and benzophenones (oxybenzone, sulisobenzone, dioxybenzone, benzoresorcinol, 2,2',4,4'-tetrahydroxybenzophenone, 2,2'-dihydroxy-4,4'-dimethoxybenzophenone, octabenzone, 4-isopropyldibenzoylmethane, butylmethoxydibenzoylmethane, etocrylene, and 4-isopropyl-dibenzoylmethane).

Particularly useful are: 2-ethylhexyl p-methoxycinnamate, 4,4'-t-butyl methoxydibenzoylmethane, 2-hydroxy-4-methoxybenzophenone, octyldimethyl p-aminobenzoic acid, digalloyltrioleate, 2,2-dihydroxy-4-methoxybenzophenone, ethyl 4-[bis(hydroxypropyl)]aminobenzoate, 2-ethylhexyl-2-cyano-3,3-diphenylacrylate, 2-ethylhexylsalicylate, glycerol p-aminobenzoate, 3,3,5-trimethylcyclohexylsalicylate, methylanthranilate, p-dimethylaminobenzoic acid or aminobenzoate, 2-ethylhexyl p-dimethylaminobenzoate, 2-phenylbenzimidazole-5-sulfonic acid, 2-(p-dimethylaminophenyl-5-sulfoniobenzoxazoic acid, and combinations thereof.

For a product marketed in the United States, preferred cosmetically-acceptable photoactive compounds and concentrations (reported as a percentage by weight of the total cosmetic sunscreen composition) include: aminobenzoic acid (also called para-aminobenzoic acid and PABA; 15% or less), avobenzone (also called butyl methoxy dibenzoylmethane; 3% or less), cinoxate (also called 2-ethoxyethyl *p*-methoxycinnamate; 3% or less), dioxybenzone (also called benzophenone-8; 3% or less), homosalate (15% or less), menthyl anthranilate (also called menthyl 2-aminobenzoate; 5% or less), octocrylene (also called 2-ethylhexyl-2-cyano-3,3 diphenylacrylate; 10% or less), octyl methoxycinnamate (7.5% or

less), octyl salicylate (also called 2-ethylhexyl salicylate; 5% or less), oxybenzone (also called benzophenone-3; 6% or less), padimate O (also called octyl dimethyl PABA; 8% or less), phenylbenzimidazole sulfonic acid (water soluble; 4% or less), sulisobenzone (also called benzophenone-4; 10% or less), titanium dioxide (25% or less), trolamine salicylate (also called triethanolamine salicylate; 12% or less), and zinc oxide (25% or less).

Other preferred cosmetically-acceptable photoactive compounds and preferred concentrations (percent by weight of the total cosmetic sunscreen composition) include diethanolamine methoxycinnamate (10% or less), ethyl-[bis(hydroxypropyl)] aminobenzoate (5% or less), glyceryl aminobenzoate (3% or less), 4-isopropyl dibenzoylmethane (5% or less), 4-methylbenzylidene camphor (6% or less), terephthalylidene dicamphor sulfonic acid (10% or less), and sulisobenzone (also called benzophenone-4, 10% or less).

For a product marketed in the European Union, preferred cosmetically-acceptable photoactive compounds and preferred concentrations (reported as a percentage by weight of the total cosmetic sunscreen composition) include: PABA (5% or less), camphor benzalkonium methosulfate (6% or less), homosalate (10% or less), benzophenone-3 (10% or less), phenylbenzimidazole sulfonic acid (8% or less, expressed as acid), terephthalidene dicamphor sulfonic acid (10% or less, expressed as acid), butyl methoxydibenzoylmethane (5% or less), benzylidene camphor sulfonic acid (6% or less, expressed as acid), octocrylene (10% or less, expressed as acid), polyacrylamidomethyl benzylidene camphor (6% or less), ethylhexyl methoxycinnamate (10% or less), PEG-25 PABA (10% or less), isoamyl p-methoxycinnamate (10% or less), ethylhexyl triazone (5% or less), drometrizole trielloxane (15% or less), diethylhexyl butamido triazone (10% or less), 4-methylbenzylidene camphor (4% or less), 3-benzylidene camphor (2% or less), ethylhexyl salicylate (5% or less), ethylhexyl dimethyl PABA (8% or less), benzophenone-4 (5%, expressed as acid), methylene bis-benztriazolyl tetramethylbutylphenol (10% or less), disodium phenyl dibenzimidazole tetrasulfonate (10% or less, expressed as acid), bis-ethylhexyloxyphenol methoxyphenol triazine (10% or less), methylene bisbenzotriazolyl tetramethylbutylphenol (10% or less, also called TINOSORB M), and bisethylhexyloxyphenol methoxyphenyl triazine.(10% or less, also called TINOSORB S).

All of the above-described UV filters are commercially available. For example, suitable commercially-available organic UV filters are identified by trade name and supplier in Table I below:

Table I

CTFA Name	Trade Name	Supplier
benzophenone-3	UVINULM-40	BASF Chemical Co.
benzophenone-4	UVINUL MS-40	BASF Chemical Co.
benzophenone-8	SPECTRA-SORB UV-24	American Cyanamid
DEA-methoxycinnamate	BERNEL HYDRO	Bernel Chemical
ethyl dihydroxypropyl-PABA	AMERSCREEN P	Amerchol Corp.
glyceryl PABA	NIPA G.M.P.A. Continued	Nipa Labs.
homosalate	KEMESTER HMS	Humko Chemical
menthyl anthranilate	SUNAROME UV-A	Felton Worldwide
octocrylene	UVINUL N-539	BASF Chemical Co.
octyl dimethyl PABA	AMERSCOL	Amerchol Corp.
octyl methoxycinnamate	PARSOL MCX	Bernel Chemical
PABA	PABA	National Starch
2-phenylbenzimidazole-5-sulphonic acid	EUSOLEX 6300	EM Industries
TEA salicylate	SUNAROME W	Felton Worldwide
2-(4-methylbenzildene)-camphor	EUSOLEX 6300	EM Industries
benzophenone-1	UVINUL 400	BASF Chemical Co.
benzophenone-2	UVINUL D-50	BASF Chemical Co.
benzophenone-6	UVINUL D-49	BASF Chemical Co.
benzophenone-12	UVINUL 408	BASF Chemical Co.
4-isopropyl dibenzoyl methane	EUSOLEX 8020	EM Industries
butyl methoxy dibenzoyl methane	PARSOL 1789 Continued	Givaudan Corp.
etocrylene	UVINUL N-35	BASF Chemical Co.
methylene bisbenzotriazolyl tetramethylbutylphenol	TINOSORB M	Ciba Specialty Chemicals
bisethylhexyloxyphenol methoxyphenyl triazine.	TINOSORB S	Ciba Specialty Chemicals

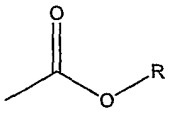
The term "alkyl" as used herein refers to straight- and branched-chain hydrocarbon groups, preferably containing one to thirty carbon atoms. Examples of alkyl groups are C_1-C_4 alkyl groups. As used herein the designation C_x-C_y, wherein x and y are integers, denotes a group having from x to y carbon atoms, *e.g.*, a C_1-C_4 alkyl group is an alkyl group having one to four carbon atoms. Nonlimiting examples of alkyl groups include,

methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl (2-methylpropyl), and t-butyl (1,1-dimethylethyl).

The term "cycloalkyl" as used herein refers to an aliphatic cyclic hydrocarbon group, preferably containing three to eight carbon atoms. Nonlimiting examples of cycloalkyl groups include cyclopropyl, cyclobutyl, cyclopentyl, and cyclohexyl.

The terms "substituted alkyl" and "substituted cycloalkyl" as used herein refer to an alkyl or cycloalkyl groups having one or more substituents. The substituents can include, but are not limited to, cycloalkyl, aryl, heteroaryl, heterocycloalkyl, substituted aryl, substituted heteroaryl, and substituted heterocycloalkyl. The preferred substituted alkyl groups have one to twenty carbon atoms, not including carbon atoms of the substituent group. Preferably, a substituted alkyl group is mono- or di-substituted at one, two, or three carbon atoms. The substituents can be bound to the same carbon or different carbon atoms.

The term "ester" as used herein refers to a group of the general formula:



wherein R is an alkyl group, cycloalkyl group, substituted alkyl group, or a substituted cycloalkyl group.

The term "aryl" as used herein refers to monocyclic, fused bicyclic, and fused tricyclic carbocyclic aromatic ring systems including, but not limited to, phenyl, naphthyl, tetrahydronaphthyl, phenanthrenyl, biphenylenyl, indanyl, indenyl, anthracenyl, and fluorenyl.

The term "heteroaryl" as used herein refers to monocyclic, fused bicyclic, and fused tricyclic aromatic ring systems, wherein one to four-ring atoms are selected from the group consisting of oxygen, nitrogen, and sulfur, and the remaining ring atoms are carbon, said ring system being joined to the remainder of the molecule by any of the ring atoms. Nonlimiting examples of heteroaryl groups include, but are not limited to, pyridyl, pyrazinyl, pyrimidinyl, pyrrolyl, pyrazolyl, imidazolyl, thiazolyl, tetrazolyl, oxazolyl, isooxazolyl,

thiadiazolyl, oxadiazolyl, thiophenyl, furanyl, quinolinyl, isoquinolinyl, benzoxazolyl, benzimidazolyl, and benzothiazolyl.

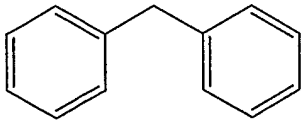
The term "heterocycloalkyl" as used herein refers to an aliphatic, partially unsaturated or fully saturated, 3- to 14-membered ring system, including single rings of 3 to 8 atoms and bi- and tricyclic ring systems. The heterocycloalkyl ring systems include one to four heteroatoms independently selected from oxygen, nitrogen, and sulfur, wherein a nitrogen and sulfur heteroatom optionally can be oxidized and a nitrogen heteroatom optionally can be substituted. Representative heterocycloalkyl groups include, but are not limited to, pyrrolidinyl, pyrazolinyl, pyrazolidinyl, imidazolinyl, imidazolidinyl, piperidinyl, piperazinyl, oxazolidinyl, isoxazolidinyl, morpholinyl, thiazolidinyl, isothiazolidinyl, and tetrahydrofuryl.

The terms "substituted aryl," "substituted heteroaryl," and "substituted heterocycloalkyl" as used herein refer to an aryl, heteroaryl, or heterocycloalkyl group substituted by a replacement of one, two, or three of the hydrogen atoms thereon with a substitute selected from the group consisting of halo, OR, $N(R)_2$, $C(=O)N(R)_2$, CN, alkyl, substituted alkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, $O(CH_2)_{1-3}N(R)_2$, $O(CH_2)_{1-3}CO_2H$, and trifluoromethyl.

The term "amino" as used herein refers an $-NH_2$ or –NH– group, wherein each hydrogen in each formula can be replaced with an alkyl, cycloalkyl, aryl, heteroaryl, heterocycloalkyl, substituted alkyl, substituted cycloalkyl, substituted aryl, substituted heteroaryl, or substituted heterocycloalkyl group, *i.e.*, $N(R)_2$. In the case of $-NH_2$, the hydrogen atoms also can be replaced with substituents taken together to form a 5- or 6-membered aromatic or non-aromatic ring, wherein one or two carbons of the ring optionally are replaced with a heteroatom selected from the group consisting of sulfur, oxygen, and nitrogen. The ring also optionally can be substituted with an alkyl group. Examples of rings formed by substituents taken together with the nitrogen atom include morpholinyl, phenylpiperazinyl, imidazolyl, pyrrolidinyl, (N-methyl)piperazinyl, and piperidinyl.

The term "cyano" as used herein refers to a $-C\equiv N$ group, also designated –CN.

The term "substituted diphenylmethylene" as used herein refers to a compound of the general formula:



wherein the compound is substituted by a replacement of one, two, or three of the hydrogen atoms resident on each aromatic ring with a substitute selected from the group consisting of halo, OR, $N(R)_2$, $C(=O)N(R)_2$, CN, alkyl, substituted alkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, $O(CH_2)_{1-3}N(R)_2$, $O(CH_2)_{1-3}CO_2H$, and trifluoromethyl.

The term "substituted 9*H*-fluorene" as used herein refers to a compound of the general formula:

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wherein the compound is substituted by a replacement of one, two, or three of the hydrogen atoms resident on each aromatic ring with a substitute selected from the group consistin g of halo, OR, $N(R)_2$, $C(=O)N(R)_2$, CN, alkyl, substituted alkyl, aryl, substituted aryl, heteroaryl, substituted heteroaryl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, $O(CH_2)_{1-3}N(R)_2$, $O(CH_2)_{1-3}CO_2H$, and trifluoromethyl.

A sunscreen composition disclosed herein can include a variety of photoactive compounds, including one or more UV-A photoactive compounds and one or more UV-B photoactive compounds. Preferably, a sunscreen composition includes a photoactive compound selected from the group consisting of p-aminobenzoic acid and salts and derivatives thereof; anthranilate and derivatives thereof; dibenzoylmethane and derivatives thereof; salicylate and derivatives thereof; cinnamic acid and derivatives thereof; dihydroxycinnamic acid and derivatives thereof; camphor and salts and derivatives thereof; trihydroxycinnamic acid and derivatives thereof; dibenzalacetone naphtholsulfonate and salts and derivatives thereof; benzalacetophenone naphtholsulfonate and salts and derivatives thereof; dihydroxy-naphthoic acid and salts thereof; o-hydroxydiphenyldisulfonate and salts and derivatives thereof; p-hydroxydiphenyldisulfonate and salts and derivatives thereof; coumarin and derivatives thereof; diazole derivatives; quinine derivatives and salts thereof;

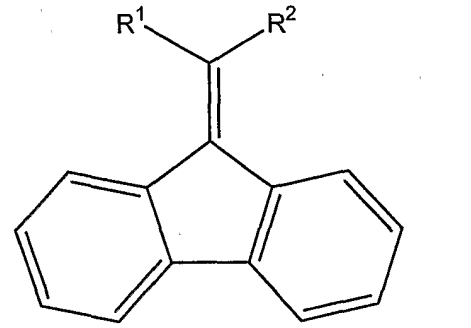
quinoline derivatives; hydroxy-substituted benzophenone derivatives; methoxy-substituted benzophenone derivatives; uric acid derivatives; vilouric acid derivatives; tannic acid and derivatives thereof; hydroquinone; benzophenone derivatives; 1,3,5-triazine derivatives, phenyldibenzimidazole tetrasulfonate and salts and derivatives thereof; terephthalylidene dicamphor sulfonic acid and salts and derivatives thereof; methylene bis-benzotriazolyl tetramethylbutylphenol and salts and derivatives thereof; bis-ethylhexyloxyphenol methoxyphenyl triazine and salts and derivatives thereof; diethylamino hydroxybenzoyl hexyl benzoate and salts and derivatives thereof; and combinations of the foregoing.

UV-A radiation (about 320 nm to about 400 nm), is recognized as contributing to causing damage, to skin particularly to very lightly-colored or sensitive skin. A sunscreen composition disclosed herein preferably includes a UV-A photoactive compound. Preferably, a sunscreen composition disclosed herein includes a dibenzoylmethane derivative UV-A photoactive compound. Preferred dibenzoylmethane derivatives include, 2-methyldibenzoylmethane; 4-methyldibenzoylmethane; 4-isopropyldibenzoylmethane; 4-tert-butyldibenzoylmethane; 2,4-dimethyldibenzoylmethane; 2,5-dimethyldibenzoylmethane; 4,4'-diisopropyldibenzoylmethane; 4,4'-dimethoxydibenzoylmethane; 4-tert-butyl-4'-methoxydibenzoylmethane; 2-methyl-5-isopropyl-4'-methoxydibenzoylmethane; 2-methyl-5-tert-butyl-4'-methoxydibenzoylmethane; 2,4-dimethyl-4'-methoxydibenzoylmethane; 2,6-dimethyl-4-tert-butyl-4'-methoxydibenzoylmethane, and combinations thereof.

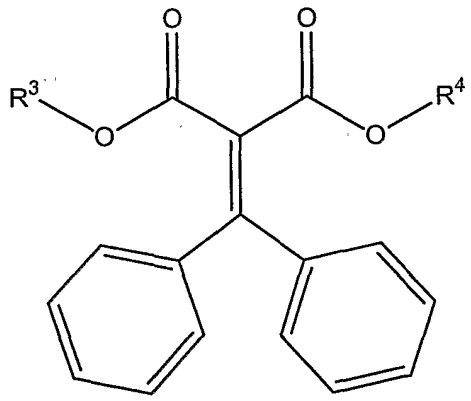
A preferred combination of photoactive compounds in a sunscreen composition includes a UV-A and a UV-B photoactive compound. However, when 2-ethylhexyl-*p*-methoxycinnamate is included in a mixture with a dibenzoylmethane derivative, the dibenzoylmethane derivative can become particularly unstable. Without intending to be limited to any particular mechanism, it is believed that the cinnamate ester reacts with an excited-state dibenzoylmethane derivative in a bimolecular pathway that renders both the dibenzoylmethane derivative and the cinnamate ester incapable of absorbing UV radiation. It has been found, quite surprisingly, that the use of one or more of a derivative of diphenylmethylenemalonic acid and derivative of fluorene (including derivatives of cyano(9H-fluoren-9-ylidene) acetic acid and diesters and polyesters of 9*H*-fluoren-9-ylidenemalonic acid) increases the stability of a sunscreen composition that includes 2-

ethylhexyl-*p*-methoxycinnamate and a dibenzoylmethane derivative. Thus, one embodiment of a sunscreen composition includes 2-ethylhexyl-*p*-methoxycinnamate, a dibenzoylmethane derivative, and one or more of a derivative of diphenylmethylenemalonic acid and a derivative of fluorene (*e.g.*, derivatives of cyano(9H-fluoren-9-ylidene) acetic acid and diesters and polyesters of 9*H*-fluoren-9-ylidenemalonic acid). Octofluorene is particularly preferred.

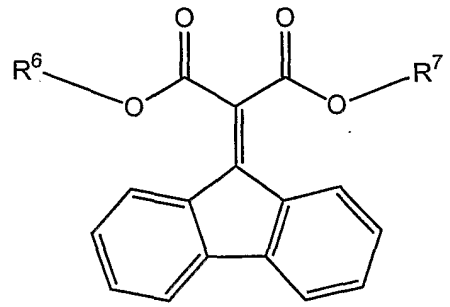
One embodiment of a sunscreen composition disclosed herein includes a mixture of a photoactive compound and a compound selected from the group consisting of compounds of formulae (I), (II), (IV) to (VI), and combinations thereof:



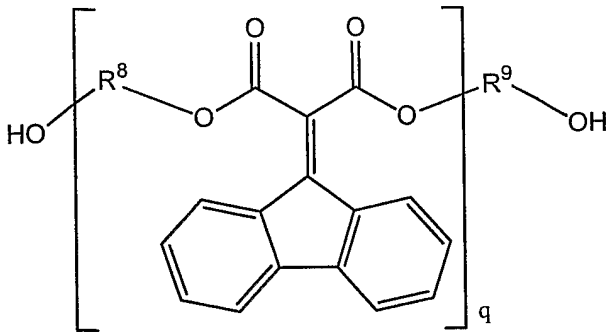
(I)



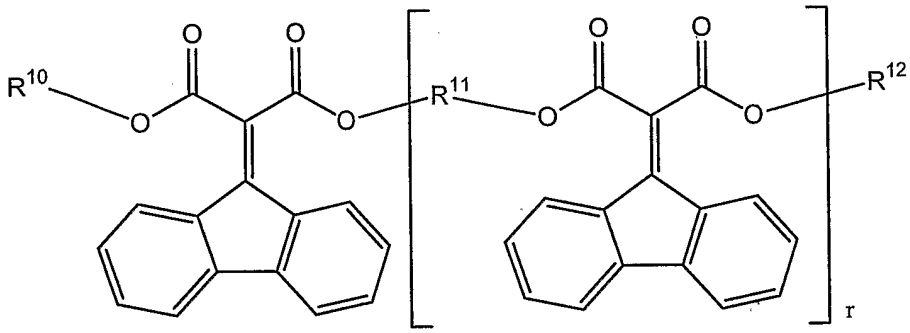
(II)



(IV)



(V)



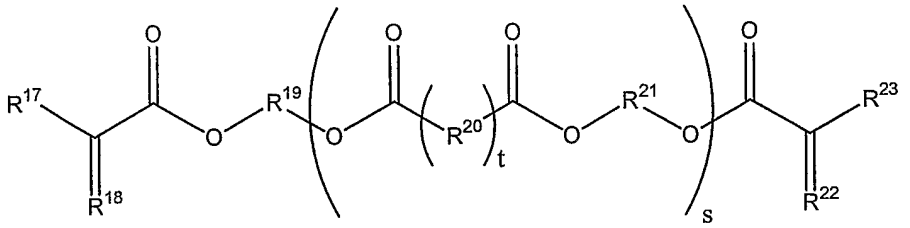
(VI)

wherein, R^1, R^2, R^3, R^4, R^6, R^7, R^8, R^9, R^{10}, R^{11}, and R^{12} are the same or different and are selected from the group consisting of C_1-C_{30} alkyl, C_3-C_8 cycloalkyl, substituted alkyl, substituted cycloalkyl, ester, aryl, heteroaryl, heterocycloalkyl, substituted aryl, substituted heteroaryl, substituted heterocycloalkyl, cyano, and amino. Compounds of formula (I), (II), and (IV) to (VI) are able to stabilize one or more photoactive compounds present in a sunscreen composition. Without intending to be limited to any particular mechanism of stabilization, it is believed that the photoactive compounds are stabilized by transferring their excited state energy (*e.g.*, singlet and triplet energy) to a derivative of diphenylmethylenemalonic acid and/or a derivative of fluorene (*i.e.*, a derivative of cyano(9H-fluoren-9-ylidene) acetic acid and a diester and/or polyester of 9*H*-fluoren-9-ylidenemalonic acid). It is believed that the transfer of excited state energy takes place because it leads to the most efficient dissipation of the excited state energy (*e.g.*, through the rapid isomerizations discussed above). Each of the R groups in a compound of formula (I) or a compound of formula (II) (R^1, R^2, R^3 and R^4) is preferably selected from C_1-C_{15} branched chain alkyls. Preferably, each of the R groups in a compound of formula (I) or a compound of formula (II) (R^1, R^2, R^3 and R^4) is 2-ethylhexane.

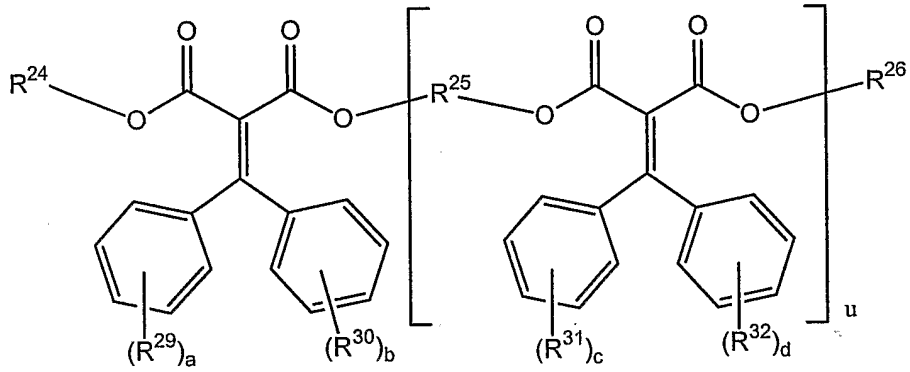
It is preferred that a compound selected from the group consisting of compounds of formulae (I), (II), (IV) to (VI), and combinations thereof, is present in a sunscreen composition in a range of about 0.1% to about 25% by weight of the total weight of the composition, more preferably about 0.1% to about 10%, still more preferably about 0.5% to about 5%.

Derivatives of fluorene, including derivatives of cyano(9H-fluoren-9-ylidene) acetic acid and diesters of diphenylmethylenemalonic acid can be prepared by a Claisen-type (Claisen-Schmidt) condensation reaction. For example, octofluorene can be prepared by reacting 2-ethylhexyl cyanoacetate with 9-fluorenone in the presence of acetic acid and sodium acetate.

Another embodiment of a sunscreen composition disclosed herein includes a mixture of a photoactive compound and a compound selected from the group consisting of compound of formula (IX) and formula (X):



(IX)



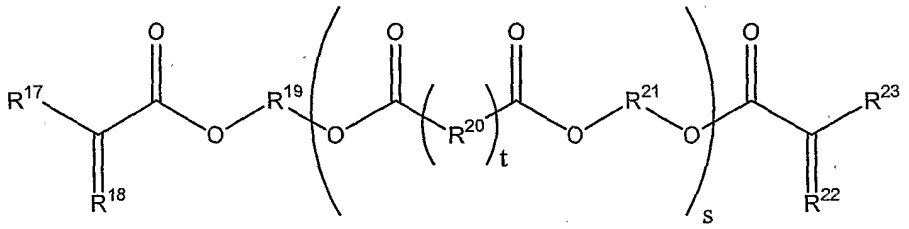
(X)

wherein, R^{19}, R^{20}, R^{21}, R^{24}, R^{25}, R^{26}, R^{29}, R^{30}, R^{31}, and R^{32} are the same or different and are selected from the group consisting of C_1-C_{30} alkyl, C_3-C_8 cycloalkyl, substituted alkyl, substituted cycloalkyl, ester, aryl, heteroaryl, heterocycloalkyl, substituted aryl, substituted heteroaryl, substituted heterocycloalkyl, and amino; R^{17} and R^{23} are the same or different and are selected from the group consisting of C_1-C_{30} alkyl, C_3-C_8 cycloalkyl, substituted alkyl, substituted cycloalkyl, ester, aryl, heteroaryl, heterocycloalkyl, substituted aryl, substituted heteroaryl, substituted heterocycloalkyl, cyano, and amino; R^{18} and R^{22} are the same or different and are selected from the group consisting of substituted diphenylmethylene, unsubstituted diphenylmethylene, substituted 9*H*-fluorene, and unsubstituted 9*H*-fluorene; t and u are each in the range of 1 to 100; s is in the range of 0 to 100; and a, b, c, and d are each in the range of 0 to 4. Compounds of formula (IX) and compounds of formula (X) are able to stabilize one or more photoactive compounds present in a sunscreen composition. Without intending to be limited to any particular mechanism of stabilization, it is believed that the photoactive compounds are stabilized by transferring their excited state energy (*e.g.*, singlet and triplet energy) to a polymer or copolymer including a 9*H*-fluorene or a diphenyl methane moiety. It is believed that the transfer of excited state energy takes place because it leads to the most efficient dissipation of the excited state energy (*e.g.*, through the rapid isomerizations discussed above). R^{19}, R^{20} and R^{21} present in a compound of formula (IX) is

preferably selected from C_1-C_{15} branched chain alkyls. It has been found that the presence of a cyano group at the terminating positions of the polymer (R^{17} and R^{23}) provides an efficient stabilization of the photoactive compound present in the composition. Without intending to be limited to a particular mechanism, it believed that the cyano group possess suitable electronic properties to allow for a speedy dissipation of energy as described above. Thus, it is preferred that R^{17} and R^{23} are the same and are cyano.

It is preferred that a compound selected from the group consisting of compounds of formula (IX) and compounds of formula (X) is present in a sunscreen composition in a range of about 0.1% to about 25% by weight of the total weight of the composition, more preferably about 0.1% to about 10%.

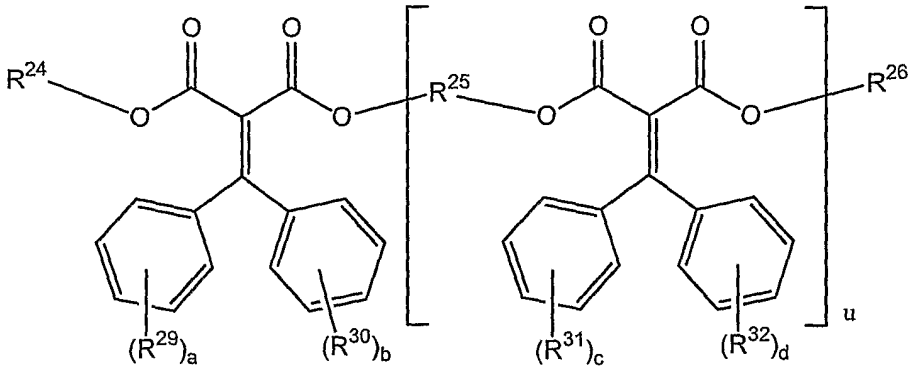
Another embodiment of the invention is a compound of formula (IX):



(IX)

wherein, R^{19}, R^{20}, and R^{21} are the same or different and are selected from the group consisting of C_1-C_{30} alkyl, C_3-C_8 cycloalkyl, substituted alkyl, substituted cycloalkyl, ester, aryl, heteroaryl, heterocycloalkyl, substituted aryl, substituted heteroaryl, substituted heterocycloalkyl, and amino; R^{17} and R^{23} are the same or different and are selected from the group consisting of C_1-C_{30} alkyl, C_3-C_8 cycloalkyl, substituted alkyl, substituted cycloalkyl, ester, aryl, heteroaryl, heterocycloalkyl, substituted aryl, substituted heteroaryl, substituted heterocycloalkyl, cyano, and amino; R^{18} and R^{22} are the same or different and are selected from the group consisting of substituted diphenylmethylene, unsubstituted diphenylmethylene, substituted 9*H*-fluorene, and unsubstituted 9*H*-fluorene; t is in the range of 1 to 100; and s is in the range of 0 to 100. Preferably, R^{19}, R^{20} and R^{21} are selected from the group consisting of C_1-C_{15} branched chain alkyls. As discussed above, preferably, R^{17} and R^{23} are the same and are cyano.

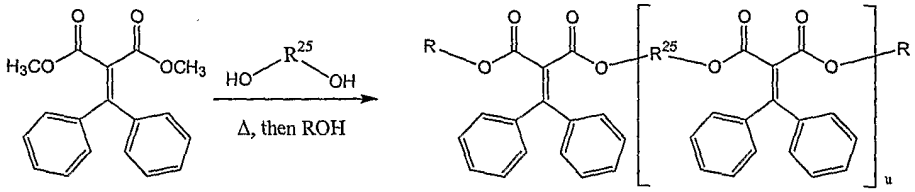
Another embodiment of the invention is a compound of formula (X):



(X)

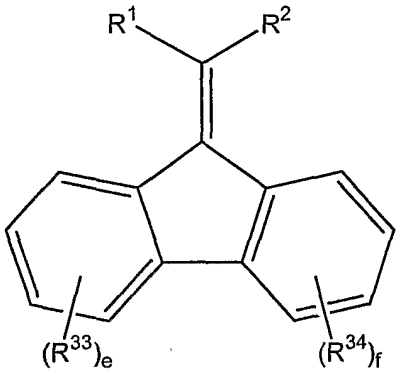
wherein R^{24}, R^{25}, R^{26}, R^{29}, R^{30}, R^{31}, and R^{32} are the same or different and are selected from the group consisting of C_1-C_{30} alkyl, C_3-C_8 cycloalkyl, substituted alkyl, substituted cycloalkyl, ester, aryl, heteroaryl, heterocycloalkyl, substituted aryl, substituted heteroaryl, substituted heterocycloalkyl, and amino; u is in the range of 1 to 100; and a, b, c, and d are each in the range of 0 to 4. Preferably, R^{24}, R^{25}, and R^{26} are selected from the group consisting of C_1-C_{15} branched chain alkyls, and also preferably, R^{24} and R^{26} are 2-ethylhexane.

Polyesters of formula (X) can be prepared by the transesterification of a diester with a diol or by the esterification of a diacid with a diol, for example as shown below for dimethyl (diphenylmethylene)malonate:

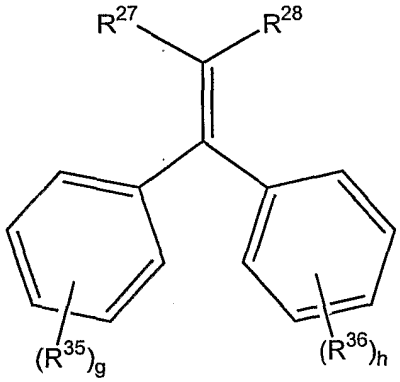


Transesterification can proceed to form a polymer under acidic, basic, or neutral conditions. When a polymer of formula (X) is prepared as shown above, the polymerization can be terminated with the addition of a compound, such as a alcohol, that cannot react any further to elongate the polymer chain. It has been found, quite surprisingly, that one or more of a compound of formula (I) and a compound of formula (XI) can be used to terminate a polymerization reaction. It has been found that one or more of a compound of formula (I) and a compound of formula (XI) can be used to terminate polymerizations of polyesters, polyamides, polyolefins, and polyurethanes, for example. Thus, another aspect of the invention is a method of making a polymer, comprising terminating a polymer chain with a

compound selected from the group consisting of compounds of formula (XII), compounds of formula (XI), and combinations thereof:



(XII)

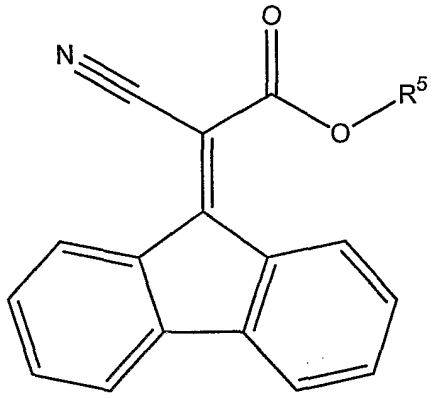


(XI)

wherein R^1 and R^{27} are cyano; R^2, R^{28}, R^{33}, R^{34}, R^{35}, and R^{36} are the same or different and are selected from the group consisting of C_1-C_{30} alkyl, C_3-C_8 cycloalkyl, substituted alkyl, substituted cycloalkyl, ester, aryl, heteroaryl, heterocycloalkyl, substituted aryl, substituted heteroaryl, substituted heterocycloalkyl, cyano, and amino; and e, f, g, h are each in the range of 0 to 4. One preferred aspect of terminating a polymerization with a compound of formula (I) and/or a compound of formula (XI) is the ability to use one or more of those polymers to increase the photostability of a photoactive compound in a sunscreen composition. Without intending to be limited to a particular mechanism, it is believed that one or more of a compound of formula (I) and formula (XI) can photostabilize a photoactive compound by a series of rapid isomerization analogous to those described above. Preferably, the polymer chain is selected from the group consisting of polyesters, polyamides, polyolefins, polyurethanes, and combinations thereof. It has been found that polymers formed according

to this method can be used to photostabilize a photoactive compound in a sunscreen composition.

Another embodiment of the invention is a compound of formula (III):



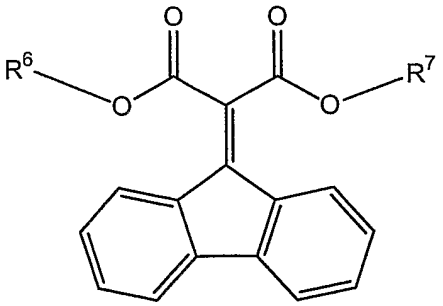
(III)

wherein R^5 is selected from the group consisting of C_3-C_{30} alkyl, C_3-C_8 cycloalkyl, substituted alkyl, substituted cycloalkyl, aryl, heteroaryl, heterocycloalkyl, substituted aryl, substituted heteroaryl, substituted heterocycloalkyl, and amino. Preferably, R^5 is a C_3-C_{20} branched chain alkyl group. More preferably, R^5 is 2-ethylhexane.

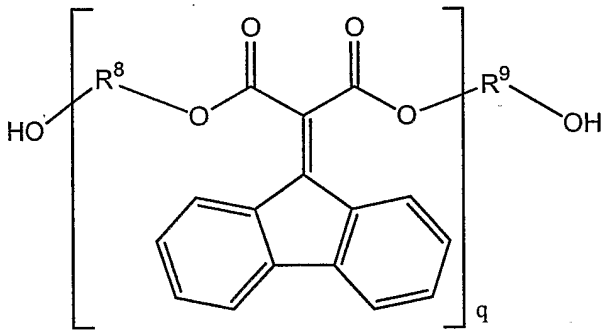
Compounds of formula (III), quite surprisingly, are able to increase the stability of a photoactive compound in a sunscreen composition. Thus, preferably, a compound of formula (III) is present in a sunscreen composition, for example, in a range of about 0.1% to about 25% by weight of the total weight of the composition, preferably in a range of about 0.1% to about 10%.

Moreover, compounds of formula (III), quite surprisingly, are intensely colored and can be used as a pigment in a paint or other application where it would be advantageous to have a coloring component present in the mixture, and would be expected to be a photostable pigment. A compound of formula (III) can also have a dual purpose in an application (*e.g.*, a paint composition) as photostabilizing one or more photoactive compounds present in the application and to impart color to the application.

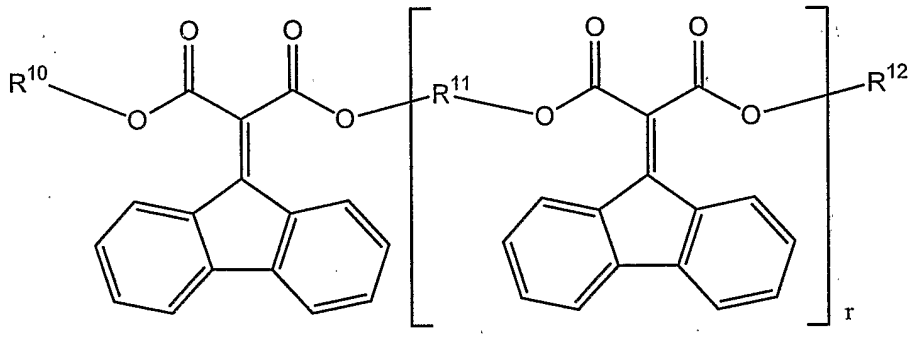
Another aspect of the invention is a compound selected from the group consisting of compounds of formula (IV) to (VI), and combinations thereof:



(IV)



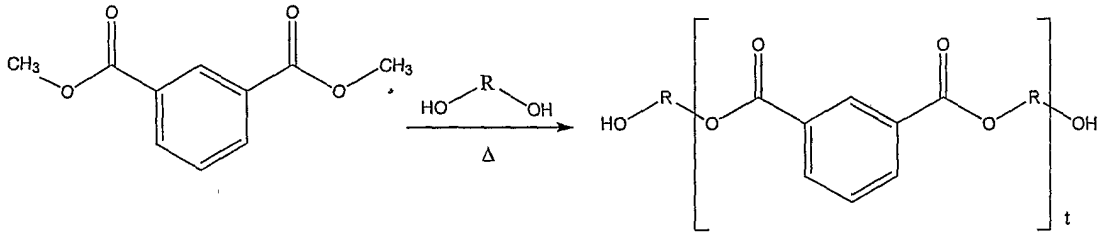
(V)



(VI)

wherein R^6 and R^7 are the same or different and are selected from the group consisting of C_3-C_{30} alkyl, C_3-C_8 cycloalkyl, substituted alkyl, substituted cycloalkyl, aryl, heteroaryl, heterocycloalkyl, substituted aryl, substituted heteroaryl, substituted heterocycloalkyl, and amino; R^8, R^9, R^{10}, R^{11}, and R^{12} are the same or different and are selected from the group consisting of C_1-C_{30} alkyl, C_3-C_8 cycloalkyl, substituted alkyl, substituted cycloalkyl, aryl, heteroaryl, heterocycloalkyl, substituted aryl, substituted heteroaryl, substituted heterocycloalkyl, and amino; and q and r are in the range of 1 to 100. Preferably, in a compound of formula (IV), R^6 and R^7 are the same and are selected from the group consisting of C_3-C_{20} branch chain alkyls. More preferably, in a compound of formula (IV), R^6 and R^7 are the same and are 2-ethylhexane.

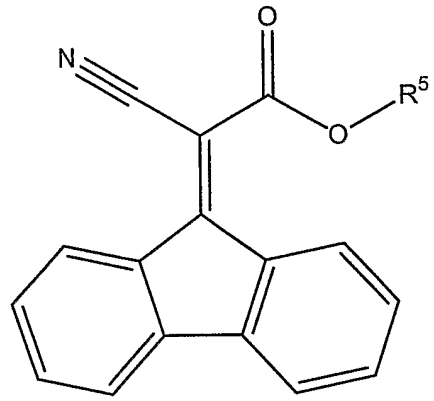
Polyesters of formula (V) and formula (VI) can be prepared by the transesterification of a diester with a diol, for example as shown below for dimethyl isophthalate:



Transesterification can proceed to form a polymer under acidic, basic, or neutral conditions.

Compounds of formulae (IV) to (VI), quite surprisingly, are able to increase the stability of a photoactive compound in a sunscreen composition. Thus, preferably, one or more of a compound of formula (IV), a compound of formula (V), and a compound of formula (VI) is present in a sunscreen composition in a range of about 0.01% to about 30% by weight of the total weight of the composition, more preferably in a range of about 0.1% to about 10%.

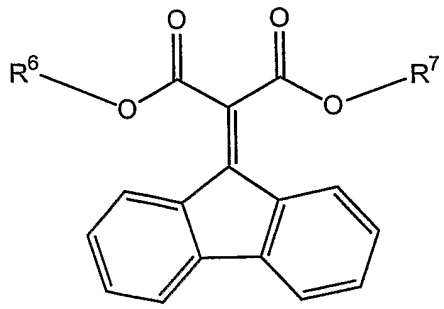
Compounds of formula (III), quite surprisingly, are able to increase the photostability of a dibenzoylmethane derivative. Without intending to be limited to a particular mechanism, it is believed that a compound of formula (III) (*e.g.*, octofluorene) stabilizes a dibenzoylmethane derivative by accepting the triplet energy of an excited state dibenzoylmethane derivative. This process of accepting the triplet excited energy of a dibenzoylmethane derivative converts the excited state dibenzoylmethane derivative to a ground state dibenzoylmethane derivative and allows the ground state dibenzoylmethane derivative to further absorb UV radiation. Thus, another embodiment of the invention is a method for photostabilizing a sunscreen composition including a dibenzoylmethane derivative, the method including the step of adding to the dibenzoylmethane derivative a photostabilizing amount of a compound of formula (III):



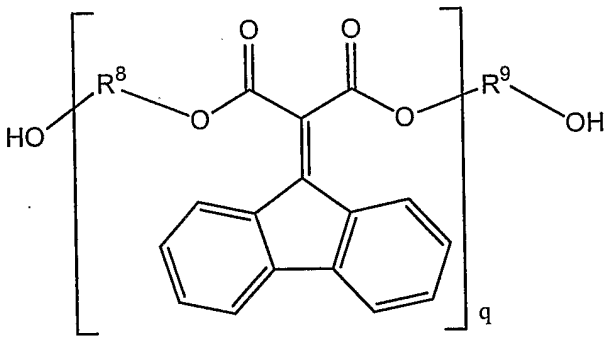
(III)

wherein, R^5 is selected from the group consisting of C_1-C_{30} straight chain alkyl, C_1-C_{30} branched chain alkyl, C_1-C_{30} alkenyl, C_1-C_{30} alkynyl, aryl, and C_3-C_8 cycloalkyl. Preferably, R^5 is selected from C_1-C_{15} branch chain alkyls. More preferably, R^5 is 2-ethylhexane. A compound of formula (III) is, preferably, present in a sunscreen that includes a dibenzoylmethane derivative in a range of about 0.1% to about 25% by weight of the total weight of the composition, more preferably in a range of about 0.1% to about 10%.

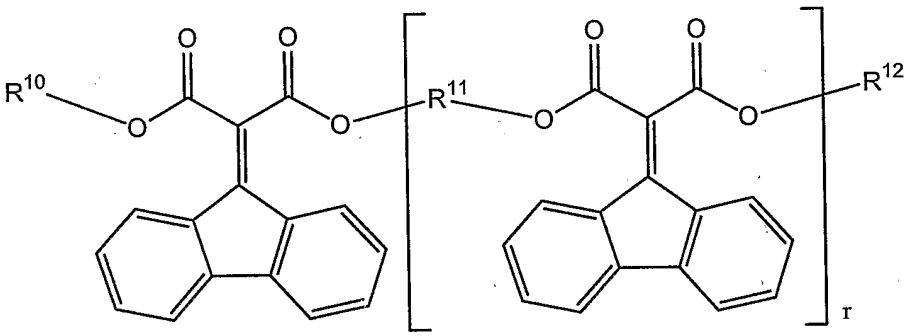
Likewise, compounds of formulae (IV) to (VI), quite surprisingly, are able to increase the photostability of a dibenzoylmethane derivative. Without intending to be limited to a particular mechanism, it is believed that a compound selected from the group consisting of compounds of formulae (IV) to (VI) is able to photostabilize a dibenzoylmethane derivative by accepting the triplet excited energy from an excited dibenzoylmethane derivative. Thus, another embodiment of the invention is a method for photostabilizing a dibenzoylmethane derivative, the method including the step of adding to the dibenzoylmethane derivative a photostabilizing amount of a compound selected from the group consisting of compounds of formulae (IV) to (VI), and combinations thereof:



(IV)



(V)



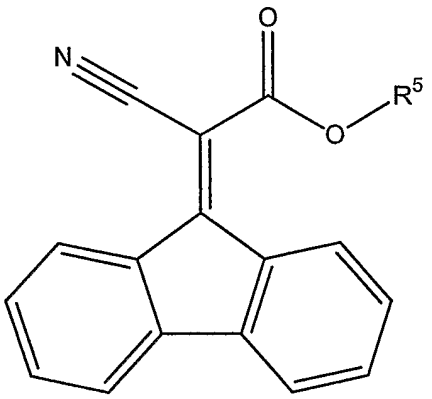
(VI)

wherein R^6, R^7, R^8, R^9, R^{10}, R^{11}, and R^{12} are the same or different and are selected from the group consisting of C_1-C_{30} alkyl, C_3-C_8 cycloalkyl, substituted alkyl, substituted cycloalkyl, aryl, heteroaryl, heterocycloalkyl, substituted aryl, substituted heteroaryl, substituted heterocycloalkyl and amino, and q and r are in the range of 1 to 100. Preferably, in a compound of formula (IV) R^6 and R^7 are the same and are selected from the group consisting of C_3-C_{20} branch chain alkyls. More preferably, in a compound of formula (IV) R^6 and R^7 are the same and are 2-ethylhexane.

A compound selected from the group consisting of compounds of formulae (IV) to (VI), and combinations thereof, preferably is present in a sunscreen composition that includes a dibenzoylmethane derivative in a range of about 0.01% to about 30% by weight of the total weight of the composition, more preferably about 0.1% to about 10%, and still more preferably about 0.5% to about 5%. Compounds of formulae (IV) to (VI), quite surprisingly, are able also to act as a photoactive compound by absorbing UV radiation. Thus, is addition to photostabilizing a photoactive compound, compounds of formulae (IV) to (VI) can protect human skin from the harmful effects of UV radiation.

Compounds of formula (III), quite surprisingly, are able also to act as a photoactive compound by absorbing UV radiation at a peak wavelength of absorbance at

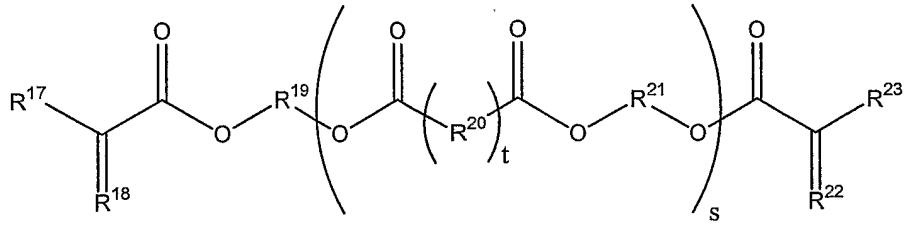
325-350 nm. Figure 1 shows the absorbance spectra for octofluorene (a compound of formula (III) wherein R^5 is 2-ethylhexane). Accordingly, another embodiment of the invention is a method of protecting human skin from ultraviolet radiation comprising topically applying to the skin, in a cosmetically acceptable carrier, a compound of formula (III):



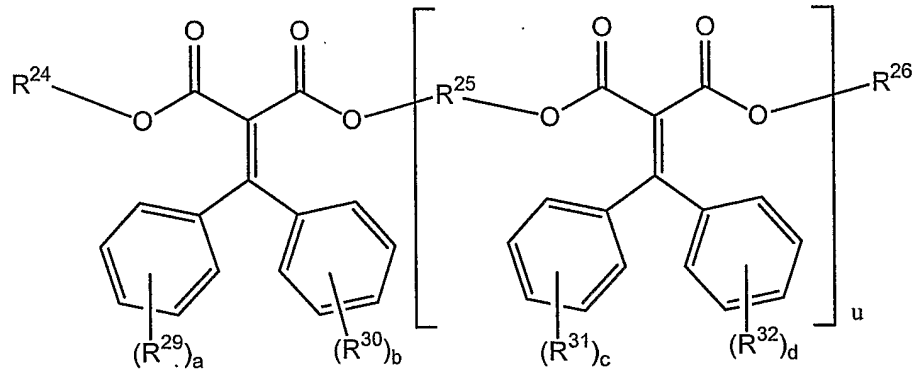
(III)

wherein, R^5 is selected from the group consisting of C_1-C_{30} alkyl, C_3-C_8 cycloalkyl, substituted alkyl, substituted cycloalkyl, aryl, heteroaryl, heterocycloalkyl, substituted aryl, substituted heteroaryl, substituted heterocycloalkyl, and amino. Preferably, R^5 is selected from C_1-C_{15} branch chain alkyls. More preferably, R^5 is 2-ethylhexane. A compound of formula (III) preferably is present a range of about 0.01% to about 25% by weight of the total weight of the composition, more preferably in a range of about 0.1% to about 10%.

It has been found, quite surprisingly, that compounds of formula (IX) and compounds of formula (X) are able also to act as a photoactive compound by absorbing UV radiation. Accordingly, another embodiment of the invention is a method of protecting human skin from ultraviolet radiation comprising topically applying to said skin, in a cosmetically acceptable carrier, a compound selected from the group consisting of compounds of formula (IX), compounds of formula (X), and combinations thereof:



(IX)



(X)

wherein, R^{19}, R^{20}, R^{21}, R^{24}, R^{25}, R^{26}, R^{29}, R^{30}, R^{31}, and R^{32} are the same or different and are selected from the group consisting of C_1-C_{30} alkyl, C_3-C_8 cycloalkyl, substituted alkyl, substituted cycloalkyl, ester, aryl, heteroaryl, heterocycloalkyl, substituted aryl, substituted heteroaryl, substituted heterocycloalkyl, and amino; R^{17} and R^{23} are the same or different and are selected from the group consisting of C_1-C_{30} alkyl, C_3-C_8 cycloalkyl, substituted alkyl, substituted cycloalkyl, ester, aryl, heteroaryl, heterocycloalkyl, substituted aryl, substituted heteroaryl, substituted heterocycloalkyl, cyano, and amino; R^{18} and R^{22} are the same or different and are selected from the group consisting of substituted diphenylmethylene, unsubstituted diphenylmethylene, substituted 9*H*-fluorene, and unsubstituted 9*H*-fluorene; t and u are each in the range of 1 to 100; s is in the range of 0 to 100; and a, b, c, and d are each in the range of 0 to 4.

EXAMPLES

The following examples are provided to illustrate the invention but are not intended to limit the scope of the invention.

Example 1

Octofluorene was prepared by placing 9-fluorenone (130.0 g, 0.721 mole, 1.0 mole equivalents), 2-ethylhexyl cyanoacetate (143.7 g, 0.728 mole, 1.01 eq), ammonium acetate (5.0 g, 0.065 mole, 0.09 eq), toluene (450 ml), and acetic acid (90 ml) into a 1 liter 3-neck round bottom flask (the reaction flask). The reaction flask was assembled with mechanical stirrer, condenser, Dean-Stark receiver, thermometer, and nitrogen inlet. The reaction mixture was then heated to reflux and water was removed continuously. The water

phase (29 ml; expected water from reaction was 13 ml) was removed and the reaction was refluxed for 18 h. When gas chromatography (GC) showed complete consumption of one of the reagents, the reaction mixture was cooled to room temperature, washed with water (2X 400 ml), diluted sodium bicarbonate (400 ml), and water (300 ml). All water washings were discarded and the organic phase was placed back in the reaction flask and all solvents were removed by distillation under vacuum. Traces of toluene were removed by steam distillation. The desired product, octofluorene, (270 g, 96% pure as determined by GC) was dried, and filtered over CELITE filter medium.

Example 2

A series of sunscreen compositions was prepared by mixing the ingredients and concentrations (formulations) shown in Table II below:

Table II

Ingredients	4% Octocrylene	4% Octofluorene
Oil Phase		
Avobenzone	2.00%	2.00%
Octyl salicylate	5.00%	5.00%
Octyl-*p*-methoxy Cinnamate	7.50%	7.50%
Octofluorene		3.60%
Octocrylene	3.60%	
C_{12}-C_{15} alkyl benzoates	10.00%	10.00%
Bodying Agent And Film-Former		
Stearyl alcohol	1.00%	1.00%
C_{30}-C_{38} olefin/Isopropyl maleate/MA copolymer	2.00%	2.00%
Emulsifiers		
Steareth 21	0.32%	0.25%
Steareth 2	0.30%	0.25%
Polyglyceryl-3 methyl glucose distearate	3.00%	3.00%
Water Phase		
Disodium EDTA	0.05%	0.05%
Glycerin	3.00%	3.00%
Methylpropanediol	2.00%	2.00%

Table II Continued

Ingredients	4% Octocrylene	4% Octofluorene
Phenoxyethanol & parabens	0.60%	0.60%
Stabilizer and Neutralizer		
Carbomer	0.20%	0.20%
Sodium hydroxide (25% solution)	0.32%	0.32%
	59.10%	

Oil-in-water emulsions were created, wherein the aqueous phase was made up of water, the water phase ingredients, the stabilizer and neutralizer, the emulsifiers, and the bodying agent and film-former listed above. The resulting sunscreens were tested for photostability by measuring absorbance on a Labsphere UV-1000S Ultraviolet Transmittance Analyzer (software version 1.27) before and after irradiation with a Solar Light Company model 16S solar simulator (equipped with a WG 320 filter to transmit radiation greater than 290 nm) in 5 MED increments up to 30 MED. Output was monitored by a PMA 2105 UV-B DCS Detector (biologically weighted) and controlled by a PMA 2100 Automatic Dose Controller (Solar Light Co.).

To test stability, a slide was positioned on the UV transmittance analyzer using registration marks, and a scan of a 1 cm spot on the slide was performed. The slide was then transferred to a holder placed adjacent to the solar simulator and, using a calipers, was positioned such that the beam of UV radiation exiting the solar simulator illuminated the same 1 cm spot on the slide. The following software settings were used: UV-B = 290–320 nm; UV-A = 320–400 nm. Following an exposure of 5 MED, the slide was again placed in position on the UV transmittance analyzer, and a scan of the exposed spot was performed. The procedure was repeated on the same 1 cm spot on the slide until the desired total radiation dosage was achieved.

Figure 3 is a graph of the percent absorbance of the sunscreen compositions listed in Table II at various intervals of exposure to radiation. As shown in figure 3, a composition including 4% octofluorene is more photostable than a composition including 4% octocrylene (after 35 MED exposure to UV radiation at a wavelength of 370 nm).

Example 4

A series of sunscreen compositions were prepared by mixing the ingredients and concentrations (formulations) shown in Table III below:

Table III

Ingredients	4% OF	4% OC	2% OF	1% OF	Control
Oil Phase					
Avobenzone	2.00%	2.00%	2.00%	2.00%	2.00%
Octyl methoxycinnamate	4.00%	4.00%	4.00%	4.00%	4.00%
Octofluorene	4.00%		2.00%	1.00%	
Octocrylene		4.00%			
C_{12}-C_{15} alkyl benzoates	10.00%	10.00%	12.00%	13.00%	14.00%
Avobenzone	2.00%	2.00%	2.00%	2.00%	2.00%
Octyl methoxycinnamate	4.00%	4.00%	4.00%	4.00%	4.00%
Bodying Agent And Film-Former					
Stearyl alcohol	1.00%	1.00%	1.00%	1.00%	1.00%
C_{30}-C_{38} olefin/Isopropyl maleate/MA copolymer	2.00%	2.00%	2.00%	2.00%	2.00%
Emulsifiers					
Steareth 21	0.30%	0.31%	0.31%	0.32%	0.32%
Steareth 2	0.20%	0.19%	0.19%	0.18%	0.18%
Polyglyceryl-3 methyl glucose distearate	3.00%	3.00%	3.00%	3.00%	3.00%
Water Phase					
Disodium EDTA	0.05%	0.05%	0.05%	0.05%	0.05%
Glycerin	3.00%	3.00%	3.00%	3.00%	3.00%
Methylpropanediol	2.00%	2.00%	2.00%	2.00%	2.00%
Phenoxyethanol & parabens	0.60%	0.60%	0.60%	0.60%	0.60%
Stabilizer and Neutralizer					
Carbomer	0.20%	0.20%	0.20%	0.20%	0.20%
Sodium hydroxide (25% solution)	0.28%	0.28%	0.28%	0.28%	0.28%
Water	67.37%	67.37%	67.37%	67.37%	67.37%

Oil-in-water emulsions were created and the stabilities of the compositions of this example were tested according to the procedures described above in Example 2.

Figure 4 is a graph of the percent absorbance of the sunscreen compositions listed in Table III at various intervals of exposure to radiation. Figure 4 shows the photostability of sunscreen compositions including various levels octocrylene and/or octofluorene. In particular, the absorbance of the sunscreen compositions at a wavelength of 310 nm was measured, which is the approximate peak absorbance for octyl-*p*-methoxy cinnamate; thus, photostability data shown in Figure 4 primarily represent the photostability of the UV-B photoactive compound, octyl-*p*-methoxy cinnamate. As discussed above, when a dibenzoylmethane derivative is combined in a sunscreen composition including octyl-*p*-methoxy cinnamate, the dibenzoylmethane derivative becomes particularly unstable. However, as shown in Figure 4, a stable sunscreen composition was formed in a composition including 4% octofluorene.

Example 5

A series of sunscreen compositions were prepared by mixing the ingredients and concentrations (formulations) shown in Table IV below:

Table IV

Ingredients	4% OF	4% OC	2% OF	1% OF	Neg.Control
Oil Phase					
Avobenzone	2.00%	2.00%	2.00%	2.00%	2.00%
Octyl-*p*-methoxy Cinnamate	4.00%	4.00%	4.00%	4.00%	4.00%
Octofluorene	4.00%		2.00%	1.00%	
Octocrylene		4.00%			
C_{12}-C_{15} alkyl benzoates	10.00%	10.00%	12.00%	13.00%	14.00%
Bodying Agent And Film-Former					
Stearyl alcohol	1.00%	1.00%	1.00%	1.00%	1.00%
C30-38 olefin/Isopropyl maleate/MA copolymer	2.00%	2.00%	2.00%	2.00%	2.00%
Emulsifiers					
Steareth 21	0.32%	0.32%	0.70%	0.70%	0.70%

Table IV Continued

Ingredients	4% OF	4% OC	2% OF	1% OF	Neg.Control
Steareth 2	0.18%	0.18%	0.40%	0.40%	0.40%
Polyglyceryl-3 methyl glucose distearate	3.00%	3.00%	3.00%	3.00%	3.00%
Water Phase					
Disodium EDTA	0.05%	0.05%	0.05%	0.05%	0.05%
Glycerin	3.00%	3.00%	3.00%	3.00%	3.00%
Methylpropanediol	2.00%	2.00%	2.00%	2.00%	2.00%
Phenoxyethanol & parabens	0.60%	0.60%	0.60%	0.60%	0.60%
Stabilizer and Neutralizer					
Carbomer	0.20%	0.20%	0.20%	0.20%	0.20%
Sodium hydroxide (25% solution)	0.28%	0.28%	0.28%	0.28%	0.28%
Water	66.37%	66.37%	59.77%	59.77%	64.77%

Oil-in-water emulsions were created and the stabilities of the compositions of this example were tested according to the procedures described above in Example 2. Figure 5 is a graph of the percent absorbance of the sunscreen compositions listed in Table IV at various intervals of exposure to radiation.

Example 6

A series of sunscreen compositions were prepared by mixing the ingredients and concentrations (formulations) shown in Table V below:

Table V

Ingredients	5% DEHN, O.45% OF	4% OC	5% DEHN	Control
Oil Phase				
Avobenzone	2.00%	2.00%	2.00%	2.00%
Octyl salicylate	5.00%	5.00%	5.00%	5.00%
Diethylhexyl 2,6-naphthalate	5.00%		5.00%	
Octofluorene	0.45%			

Table V Continued

Ingredients	5% DEHN, O.45% OF	4% OC	5% DEHN	Control
Octocrylene		4.00%		
C_{12}-C_{15} alkyl benzoates		10.00%	10.00%	10.00%
Octyldodecyl neopentanoate			5.00%	
Polyisobutene				5.00%
Diethylhexyl malate	9.55%			
Bodying Agent And Film-Former				
Stearyl alcohol	1.00%	1.00%	1.00%	1.00%
C_{30}-C_{38} olefin/Isopropyl maleate/MA copolymer	2.00%	2.00%	2.00%	2.00%
Emulsifiers				
Steareth 21	0.32%	0.32%	0.70%	0.70%
Steareth 2	0.18%	0.18%	0.40%	0.40%
Polyglyceryl-3 methyl glucose distearate	3.00%	3.00%	3.00%	3.00%
Water Phase				
Disodium EDTA	0.05%	0.05%	0.05%	0.05%
Glycerin	3.00%	3.00%	3.00%	3.00%
Methylpropanediol	2.00%	2.00%	2.00%	2.00%
Phenoxyethanol & parabens	0.60%	0.60%	0.60%	0.60%
Stabilizer and Neutralizer				
Carbomer	0.20%	0.20%	0.20%	0.20%
Sodium hydroxide (25% solution)	0.28%	0.28%	0.28%	0.28%
Water	65.37%	66.37%	59.77%	64.77%

Oil-in-water emulsions were created and the stabilities of the compositions of this example were tested according to the procedures described above in Example 2.

Figure 6 is a graph of the percent absorbance of the sunscreen compositions listed in Table V at various intervals of exposure to radiation. This figure shows the increase in stability of absorbance at 370 nm by the addition of very low levels of octofluorene to a composition including avobenzone and 5% by weight of diethylhexyl naphthalate (DEHN).

Without intending to be limited to a particular mechanism of action, it is believed that in a composition including a diester or polyester of naphthalene dicarboxylic acid compound such as DEHN and a derivative of fluorene, depending on the concentrations of the derivative of fluorene, one of the compounds would exclusively dominate the photostability profile. Thus, one would expect that at high concentration of a diester or polyester of naphthalene dicarboxylic acid compound, the addition of low and very low levels of one or more derivatives of fluorene would not increase the overall photostability of the dibenzoylmethane derivative.

It has been found, quite surprisingly however, that at low (*e.g.*, 1% by weight) and very low levels (*e.g.*, less that 0.5% by weight) of a derivative of fluorene, the combination can work synergistically to provide even greater stabilization of a dibenzoylmethane derivative than would be expected. Without intending to be limited to any particular mechanism of operation, it is believed that the relatively high concentration of diester or polyester of naphthalene dicarboxylic acid provides a sufficient amount of the diesters or polyesters in proximity to dibenzoylmethane derivatives and, as the dibenzoylmethane derivatives are excited to their triplet excited states, the diester or polyester accepts the triplet excited energy at a sufficient rate to substantially reduce or prevent degradation of the dibenzoylmethane derivative.

At the same time, however, the relatively low amount of a derivative of fluorene is believed to rapidly accept triplet excited energy from the relatively numerous diester or polyester molecules around it in solution, and very rapidly dissipate the energy through a rapid isomerization mechanism, thus generating ground state diesters or polyesters of naphthalene dicarboxylic acid that are once again able to accept excited state energy from an excited dibenzoylmethane derivative. Thus, the weight ratio of dibenzoylmethane derivative to a derivative of fluorene is, preferably, at least about 6:1, for example at least 10:1.

In addition, as shown in Figure 6, a stable composition was formed in a composition including low levels of octofluorene and 5% by weight of DEHN.

Example 7

A series of sunscreen compositions were prepared by mixing the ingredients and concentrations (formulations) shown in Table VI below:

Table VI

Ingredients	5% DEHN, O.45% OF	4% OC	5% DEHN, 0.45% OC	5% DEHN Alone	D.C. Adjust-ment Alone	Control
Oil Phase						
Avobenzone	2.00%	2.00%	2.00%	2.00%	2.00%	2.00%
Octyl salicylate	5.00%	5.00%	5.00%	5.00%	5.00%	5.00%
Diethylhexyl 2,6-naphthalate	5.00%		5.00%	5.00%		
Octofluorene	0.45%					
Octocrylene		4.00%	0.45%			
C_{12}-C_{15} alkyl benzoates		10.00%		10.00%		10.00%
Octyldodecyl neopentanoate				5.00%		
Polyisobutene						5.00%
Diethylhexyl malate	9.55%		9.55%		10.00%	
Butyloctyl dimer with HDI					5.00%	
Bodying Agent And Film-Former						
Stearyl alcohol	1.00%	1.00%	1.50%	1.00%	1.20%	1.00%
C_{30}-C_{38} olefin/Isopropyl maleate/MA copolymer	2.00%	2.00%	2.00%	2.00%	2.00%	2.00%
Emulsifiers						
Steareth 21	0.32%	0.32%	0.33%	0.70%	0.55%	0.70%
Steareth 2	0.18%	0.18%	0.18%	0.40%	0.7%	0.40%
Polyglyceryl-3 methyl glucose distearate	3.00%	3.00%	3.00%	3.00%	3.00%	3.00%
Water Phase						
Disodium EDTA	0.05%	0.05%	0.50%	0.05%	5.00%	0.05%
Glycerin	3.00%	3.00%	3.00%	3.00%	3.00%	3.00%
Methylpropanediol	2.00%	2.00%	2.00%	2.00%	2.00%	2.00%
Phenoxyethanol & parabens	0.60%	0.60%	0.60%	0.60%	0.60%	0.60%
Stabilizer and Neutralizer						
Carbomer	0.20%	0.20%	0.20%	0.20%	0.20%	0.20%

Table VI

Ingredients	5% DEHN, O.45% OF	4% OC	5% DEHN, 0.45% OC	5% DEHN Alone	D.C. Adjust-ment Alone	Control
Sodium hydroxide (25% solution)	0.28%	0.28%	0.29%	0.28%	0.28%	0.28%
Water	65.37%	66.37%	64.40%	59.77%	59.47%	64.77%

Oil-in-water emulsions were created and the stabilities of the compositions of this example were tested according to the procedures described above in Example 2.

Figure 7 is a graph of the percent absorbance of the sunscreen compositions including various combinations of octocrylene, octofluorene, and DEHN as listed in Table VI and at various intervals of exposure to radiation. As described in Example 6, it has been found, quite surprisingly, that at low (*e.g.*, 1% by weight) and very low levels (*e.g.*, less than 0.5% by weight) of a derivative of fluorene, the combination works synergistically to provide even greater stabilization of a dibenzoylmethane derivative than would be expected. As shown in Figure 7, a stable sunscreen composition was formed by the combination of 5% DEHN and 0.45% of octofluorene into a sunscreen composition.

Example 8

A series of sunscreen compositions were prepared by mixing the ingredients and concentrations (formulations) shown in Table VII below:

Table VII

Ingredients	1% DPFM	2% DPFM	3% DPFM	Control
Oil phase				
Avobenzone	2.00%	2.00%	2.00%	2.00%
Octyl salicylate	5.00%	5.00%	5.00%	5.00%
Diisopropyl fluorenmalonate	1.00%	2.00%	3.00%	
C_{12}-C_{15} alkyl benzoates	14.00%	13.00%	12.00%	10.00%
Polyisobutene				5.00%
Dimethyl capramide			1.00%	
Bodying Agent And Film-Former				
Stearyl alcohol	1.00%	1.00%	1.00%	1.00%
C_{30}-C_{38} olefin/Isopropyl maleate/MA copolymer	2.00%	2.00%	2.00%	2.00%

Table VII Continued

Emulsifiers				
Steareth 21	0.38%	0.28%	0.28%	0.70%
Steareth 2	0.18%	0.22%	0.22%	0.40%
Polyglyceryl-3 methyl glucose distearate	3.00%	3.00%	3.00%	3.00%
Water Phase				
Disodium EDTA	0.05%	0.05%	0.05%	0.05%
Glycerin	3.00%	3.00%	3.00%	3.00%
Methylpropanediol	2.00%	2.00%	2.00%	2.00%
Phenoxyethanol & parabens	0.60%	0.60%	0.60%	0.60%
Stabilizer and Neutralizer				
Carbomer	0.20%	0.20%	0.20%	0.20%
Sodium hydroxide (25% solution)	0.28%	0.28%	0.28%	0.28%
Water	65.31%	65.37%	64.37%	64.77%

Oil-in-water emulsions were created and the stabilities of the compositions of this example were tested according to the procedures described above in Example 2.

Figure 8 is a graph of the percent absorbance of the sunscreen compositions listed in Table VII at various intervals of exposure to radiation. Figure 8 shows the photostability of sunscreen compositions including various levels of diisopropyl fluorenmalonate (diisopropyl 9*H*-fluoren-9-ylidenemalonate, a compound of formula IV wherein R^6, R^7 are the same and are isopropane). As shown in figure 8, as the amount of diisopropyl fluorenmalonate is increased, the photostability of the photoactive compounds in the composition (*e.g.*, avobenzone) increases.

SYNTHESIS OF UV ACTIVE 2-CYANO-3,3-DIPHENYLACRYLATE-TERMINATED POLYMERS (CP)

Linear Synthesis : General Procedure:

Methyl 2-cyano-3,3-diphenylacrylate (1 mole equivalent) is dissolved in an excess of 2-methylpropane-1,3-diol (from 2 to 15 mole equivalents) placed in 3-neck round bottom flask, and sodium carbonate (0.01 up to 0.9 mole equivalents) is added. Next, the reaction mixture is heated to 130°C (optimum temperature may very from 130°C to 150°C depending on the type of methyl ester). Throughout reaction time, methanol is removed from the reaction mixture by continuous distillation. When the reaction is completed (within one or two hours), sodium carbonate is filtered off and the crude product is cooled to room

temperature and dissolved in ethyl acetate. The ethyl acetate solution is washed several times with water to remove completely the excess glycol. Ethyl acetate is then removed by distillation and the product is dried under vacuum. GC analysis shows only desired product present, which is used without any further purification in synthesis of all polymers and monomers.

The following problems were encountered and solved during the linear synthesis of the 2-cyano-3,3 diphenylacrylate-terminated polymers:

1. The final step, the benzophenone and 9-fluorenone condensations with cyanoacetate-terminated polymer, proceeds with only 70-90% completion. This leaves 10-30% of free ketone still present in the product. A better synthetic path, which will allow complete incorporation of the ketone into a polymer, is desirable.

2. One of the reasons for the incomplete reaction is the fact that the rate-determining step is reversible to some extent. Also, the rate of ketone condensation with cyanoacetate is comparable with the aldol-type condensation of the cyanoacetate moiety with any ester functionality of the polymer. This was proven by using PEG polymer, which was terminated with cyanoacetic acid and then reacted with the ketone.

New and more efficient ways of synthesis of the UV active polymers are as follows:

Method Of Terminating Polymers On Both Ends With 2-Cyano-3,3-Diphenylacrylate (2-cyano-3,3-diphenyl-2-propenoate):

Procedure 1: Using Polymer Terminated With Acid Functionality:

Designed polymer (1 mole equivalent; **(Note 1)** and 3-hydroxy-2-methylpropyl 2-cyano-3,3-diphenylacrylate (1.9 mole equivalents) were dissolved in xylenes **(Note 2)** and methanesulfonic acid (from 0.05 up to 0.3 mole equivalents; **(Note 3)** was added. The reaction mixture was heated to reflux and water was removed azeotropically using Dean-Stark receiver. According to GPC results, the reaction was completed within 2 hours and 30 minutes, when vacuum was applied to remove xylenes. The crude product was dissolved in ethyl acetate, washed with water (two times), diluted with sodium bicarbonate solution (one time), and again with water (one time). The ethyl acetate solution was returned

to the reaction flask and all solvents were removed using simple distillation with applied vacuum (**Note 4**). The still hot product was filtered through Celite.

Procedure 2: Using Polymer Terminated With Hydroxyl Functionality:

Designed polymer (1 mole equivalent, **Note 1**) is first refluxed at (130-140°C) in xylenes (**Note 2**) for 30 minutes to remove any moisture present in the polymer. The solution is then cooled to 80°C and acid anhydride (2.02 mole equivalents) is added, the reaction mixture is allowed to react for up to 20 minutes and 3-hydroxy-2-methylpropyl 2-cyano-3,3-diphenylacrylate (1.9 mole equivalents) is added followed by methanesulfonic acid (from 0.05 up to 0.3 mole equivalents; (**Note 3**). The reaction mixture is then refluxed for one hour (when GPC confirms completion of the reaction) and vacuum is applied to remove xylenes. Workup of final product is done as in Procedure 1 (**Note 4**).

Note 1: Polymer is designed according to one's needs, having the acid at the terminal position by using an excess of diacid, or hydroxyl group, by using an excess of glycol.

Note 2: The amount of xylenes used is adjusted to the reaction scale. On larger scales, a minimum amount of xylenes as solvent can be used to solvate the reactants, especially when the starting materials are solids.

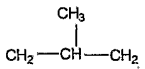
Note 3: When a large amount of solvent is used, a larger amount of catalyst can be used to drive the reaction to completion in a reasonable time.

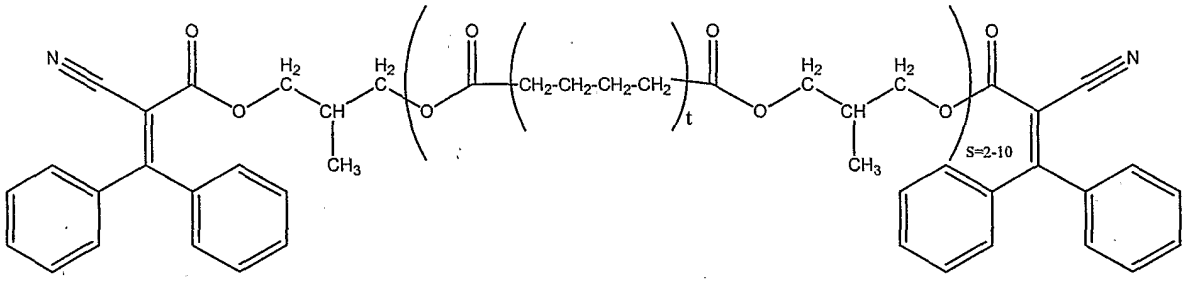
Note 4: Xylenes and ethyl acetate solvents can be recycled when the reaction is done on a commercial scale.

Example 9

A photoactive polymer of the general structure of formula (IX) was prepared by placing adipic acid (3 times the "s" molar equivalent) and methylpropanediol (4 times the "s + 1" molar equivalent) in a 2 liter 3-neck round bottom flask (the reaction flask). The reaction flask was assembled with a simple distillation apparatus and the reaction mixture was heated up to 210 °C until a condensation reaction between the diacid (adipic acid) and the diol (methylpropanediol) was completed. The reaction flask was then cooled down to

160 °C and cyanoacetic acid (2 moles) was added and a condensation reaction between the polyester that was formed and the cyano acetic acid was completed. The polymer was then cooled to room temperature and transferred to a 3 liter round bottom flask and 9-fluorenone (2 mole equivalent) was added, followed by the addition of toluene (1000 ml), acetic acid (220 ml), and ammonium acetate (0.1 to 0.3 mole). The reaction was then heated to reflux for 24 hours and the product was cooled to room temperature. The reaction mixture was then sequentially washed with water (1000 ml), sodium bicarbonate (600 ml), brine (1000 ml), and water (1000 ml). The organic layer was then stripped of all solvents and dried under vacuum. The reaction produced an 85% yield of polymer.

In the following Tables VIII, IX and X (Examples 10, 11 and 12), the CP copolymer is the copolymer defined by formula IX, wherein R^{17} and R^{23} are cyano; R^{18} and R^{22} are diphenylmethylene; R^{19} and R^{21} are: 
R^{20} is CH_2-CH_2-CH_2-CH_2; t=1 and s= 2-10, as follows:



Example 10

A series of sunscreen compositions was prepared by mixing the ingredients and concentrations (formulations) shown in Table VIII below:

Table VIII

Ingredients	Non-Irradiated Control	Polymer + Napthalate	Napthalate	Negative Control
Oil phase				
Avobenzone	3.00%	3.00%	3.00%	2.00%
Octyl salicylate	5.00%	5.00%	5.00%	5.00%
Homosalate	5.00%	5.00%	5.00%	0.00%

Table VIII

Ingredients	Non-Irradiated Control	Polymer + Napthalate	Napthalate	Negative Control
Diethylhexyl 2,6-naphthalate (DEHN)	7.50%	7.50%	7.50%	0.00%
Hexanedioic acid polymer with 2-methyl-2,3-propanediol, bis(2-cyano-3,3-diphenyl-2-propenoate) (CP)	1.00%	1.00%	0.00%	0.00%
Dimethyl capramide	1.00%	1.00%	1.00%	0.00%
Butyloctyl salicylate	3.50%	3.50%	4.50%	0.00%
Polyisobutene	0.00%	0.00%	0.00%	5.00%
C_{12}-C_{15} alkyl benzoates	0.00%	0.00%	0.00%	10.00%
Dimethicone	0.00%	0.00%	0.00%	0.25%
Bodying agent and film-former				
Stearyl alcohol	1.00%	1.00%	1.00%	1.00%
C_{30}-C_{38} olefin/Isopropyl maleate/MA copolymer	2.00%	2.00%	2.00%	2.00%
Emulsifiers				
Steareth 21	0.31%	0.31%	0.31%	0.70%
Steareth 2	0.19%	0.19%	0.19%	0.40%
Polyglyceryl-3 methyl glucose distearate	3.00%	3.00%	3.00%	3.00%
Water phase				
Disodium EDTA	0.05%	0.05%	0.05%	0.05%
Glycerin	4.00%	4.00%	4.00%	3.00%
Methylpropanediol	0.00%	0.00%	0.00%	2.00%
Phenoxyethanol & parabens	0.60%	0.60%	0.60%	0.60%
Stabilizer and neutralizer				
Carbomer	0.20%	0.20%	0.20%	0.20%
Sodium hydroxide (25% solution)	0.28%	0.28%	0.28%	0.28%
Water	62.37%	62.37%	62.37%	64.52%

Continued

Oil-in-water emulsions were created, wherein the aqueous phase was made up of water, the water phase ingredients, the stabilizer and neutralizer, the emulsifiers, and the bodying agent and film-former listed above. The resulting sunscreens were tested for photostability by measuring absorbance on a Labsphere UV-1000S Ultraviolet Transmittance Analyzer (software version 1.27) before and after irradiation with a Solar Light Company

model 16S solar simulator (equipped with a WG 320 filter to transmit radiation greater than 290 nm) in 5 MED increments up to 35 MED. Output was monitored by a PMA 2105 UV-B DCS Detector (biologically weighted) and controlled by a PMA 2100 Automatic Dose Controller (Solar Light Co.). After the composition had been exposed to 35 MED of irradiation, the absorbance of each composition was measured between 280 nm and 400 nm (the UV-B range). The resulting absorbance spectra are shown in Figure 9.

In addition to the level of absorbance for each composition in the UV-B range, the absorption spectra also indicate the stability of each composition after irradiation at 35 MED. The stability of the composition can be measured against the control composition (non-irradiated control), which was not exposed to any irradiation. Figure 9 shows an increase in the photostability with the addition of 1% by weight of the Crylene Polymer (Hexanedioic acid, polymer with 2-methyl-2,3-propanediol, bis(2-cyano-3,3-diphenyl-2-propenoate)) to a composition including 7.5% by weight of diethylhexyl 2,6-naphthalate.

Example 11

A series of sunscreen compositions were prepared by mixing the ingredients and concentrations (formulations) shown in the following Table IX to show synergy between CP and DEHN at stabilizing dibenzoylmethane derivatives, such as avobenzone:

Table IX

Ingredients	5% DEHN/ 4% CP	5% DEHN/ 2% CP	4% CP	5% DEHN/ .5% CP	2% CP	7.5% DEHN	Neg. Control
Oil phase							
Avobenzone	3.00%	3.00%	3.00%	3.00%	3.00%	3.00%	2.00%
Octyl salicylate	5.00%	5.00%	5.00%	5.00%	5.00%	5.00%	5.00%
Homosalate	5.00%	5.00%	5.00%	5.00%	5.00%	5.00%	0.00%
Diethylhexyl 2,6-naphthalate (DEHN)	5.00%	5.00%	0.00%	5.00%	0.00%	7.50%	0.00%
Hexanedioic acid, polymer with 2-methyl-2,3-propanediol, bis(2-cyano-3,3-diphenyl-2-propenoate) (CP)	4.00%	2.00%	4.00%	0.50%	2.00%	0.00%	0.00%
Diethylhexyl malate	0.00%	2.00%	9.00%	2.00%	11.00%	4.56%	0.00%
Dimethyl capramide	1.00%	1.00%	1.00%	1.00%	1.00%	1.00%	0.00%
Butyloctyl salicylate	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	10.00%
Polyisobutene	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	5.00%

Table IX

Ingredients	5% DEHN/ 4% CP	5% DEHN/ 2% CP	4% CP	5% DEHN/ .5% CP	2% CP	7.5% DEHN	Neg. Control
Bodying agent and film-former							
Stearyl alcohol	1.00%	1.00%	1.00%	1.00%	1.00%	1.00%	1.20%
C_{30}-C_{38} olefin/Isopropyl maleate/MA copolymer	2.00%	2.00%	2.00%	2.00%	2.00%	2.00%	2.00%
Emulsifiers							
Steareth 21	0.29%	0.30%	0.29%	0.29%	0.30%	0.31%	0.70%
Steareth 2	0.21%	0.20%	0.21%	0.21%	0.20%	0.19%	0.40%
Polyglyceryl-3 methyl glucose distearate	3.00%	3.00%	3.00%	3.00%	3.00%	3.00%	3.00%
Water phase							
Disodium EDTA	0.05%	0.05%	0.05%	0.05%	0.05%	0.05%	0.05%
Glycerin	3.00%	3.00%	4.00%	3.00%	4.00%	3.00%	3.00%
Methylpropanediol	2.00%	2.00%	0.00%	2.00%	0.00%	2.00%	2.00%
Phenoxyethanol & parabens	0.60%	0.60%	0.60%	0.60%	0.60%	0.60%	0.60%
Stabilizer and neutralizer							
Carbomer	0.20%	0.20%	0.20%	0.20%	0.20%	0.20%	0.20%
Sodium hydroxide (25% solution)	0.28%	0.28%	0.28%	0.28%	0.28%	0.28%	0.04%
Water	64.37%	64.37%	61.37%	65.87%	61.37%	61.31%	64.81%

Continued

The oil-in-water emulsions shown in Table IX were created, wherein the aqueous phase was made up of water, the water phase ingredients, the stabilizer and neutralizer, the emulsifiers, and the bodying agent and film-former listed above. The resulting sunscreens were tested for photostability by measuring absorbance on a Labsphere UV-1000S Ultraviolet Transmittance Analyzer (software version 1.27) before and after irradiation with a Solar Light Company model 16S solar simulator (equipped with a WG 320 filter to transmit radiation greater than 290 nm) in 5 MED increments up to 35 MED. Output was monitored by a PMA 2105 UV-B DCS Detector (biologically weighted) and controlled by a PMA 2100 Automatic Dose Controller (Solar Light Co.). After the composition had been exposed to 35 MED of irradiation, the absorbance of each composition was measured between 280 nm and 400 nm (the UV-B range). The resulting absorbance spectra are shown

in Figure 10. The formulation of Table IX was also tested, in the same manner, using UV-A radiation (320 nm to 400 nm). The resulting absorbance spectra are shown in Figure 11.

In addition to the level of absorbance for each composition in the UV-A and UV-B ranges, the absorption spectra also indicate the stability of each composition after irradiation at 35 MED. The stability of the composition can be measured against the negative control composition containing no CP and no DEHN and to the composition (O MED) which was not exposed to any irradiation. Figures 10 and 11 show an increase in the photostability with the addition of 2% by weight of Hexanedioic acid, polymer with 2-methyl-2,3-propanediol, bis(2-cyano-3,3-diphenyl-2-propenoate) (CP) to a composition including 5.0% by weight of diethylhexyl 2,6-naphthalate (DEHN), in both the UV-A and UV-B ranges.

Surprisingly, the combination of 5% DEHN and 2% CP is just as effective at stabilizing avobenzone as the combination of 5% DEHN and 4% CP; both combinations are better than 4% CP alone; and 2% CP is just as good as 7.5% DEHN at stabilizing avobenzone, after irradiation with both UV-A and UV-B.

Amounts of copolymer (CP) as low as 0.1%, preferably at least 0.2%, are sufficient to form a synergistic combination with one or more diesters and/or polyesters of naphthalene dicarboxylic acid, *e.g.*, DEHN, to photostabilize a sunscreen composition containing a UV-absorbent sunscreen compound, particularly a dibenzoylmethane derivative, such as avobenzone. The amount of the copolymer (CP) should be in the range of about 0.1% to about 15% by weight of the sunscreen formulation, preferably about 0.2% to about 10% by weight, more preferably about 0.3% to about 5% by weight of the sunscreen formulation. The amount of the diester or polyester of naphthalene dicarboxylic acid should be in the range of about 2% to about 15% by weight of the sunscreen formulation, preferably about 4% to about 10% by weight, more preferably about 4% to about 8% by weight of the sunscreen formulation.

As shown in the data of Table IX and in the graphs of Figures 10 and 11, the copolymer (CP) and diesters or polyesters of naphthalene dicarboxylic acid (DEHN) act synergistically to photostabilize avobenzone. The amount of CP should be at least 2% by weight based on the weight of DEHN, *e.g.*, at least 0.1% CP in a formulation containing 5.0%

by weight DEHN. The weight ratio of the copolymer (CP) to the diester or polyester of naphthalene dicarboxylic acid, *e.g.*, DEHN should be in the range of about 0.02 to about 5.0, preferably about 0.02 to 1.5, more preferably about 0.05 to 1.0, even more preferably about 0.1 to about 0.75.

Another series of sunscreen compositions was prepared by mixing the ingredients and concentrations (formulations) shown in the following Table X to show synergy between CP and oxybenzone at photostabilizing dibenzoylmethane derivatives, such as avobenzone.

TABLE X

Ingredients	4% CP, 4 Oxy	4% CP	2% CP
Oil phase			
Avobenzone	3.00%	3.00%	3.00%
Oxybenzone	4.00%	0.00%	0.00%
Octyl salicylate	5.00%	5.00%	5.00%
Homosalate	7.50%	5.00%	5.00%
Hexanedioic acid polymer with 2-methly-2,3-propanediol, bis(2-cyano-3,3-diphenyl-2-propenoate) (CP)	4.00%	4.00%	2.00%
Diethylhexyl malate	2.00%	9.00%	11.00%
C12-15 alkyl benzoates	0.00%	0.00%	0.00%
Polyisobutene	0.00%	0.00%	0.00%
Dimethyl capramide	1.00%	1.00%	1.00%
Bodying agent and film-former			
Stearyl alcohol	1.00%	1.00%	1.00%
C30-38 olefin/Isopropyl maleate/MA copolymer	2.00%	2.00%	2.00%
Emulsifiers			
Steareth 21	0.30%	0.29%	0.30%
Steareth 2	0.20%	0.21%	0.20%
Polyclyceryl-3 methyl glucose distearate	3.00%	3.00%	3.00%
Water phase			
Disodium EDTA	0.05%	0.05%	0.05%
Glycerine	3.00%	4.00%	4.00%
Methylpropanediol	2.00%	0.00%	0.00%
Phenoxyethanol & parabens	0.60%	0.60%	0.60^
Stabilizer and neutralizer			
Carbomer	0.20%	0.20%	0.20%
Sodium hydroxide (25%)	0.28%	0.28%	0.28%
Water	60.87%	61.37%	61.37%

The oil-in-water emulsions shown in Table X were created, wherein the aqueous phase was made up of water, the water phase ingredients, the stabilizer and neutralizer, the emulsifiers, and the bodying agent and film-former listed above. The resulting sunscreens were tested for photostability by measuring absorbance on a Labsphere UV-1000S Ultraviolet Transmittance Analyzer (software version 1.27) before and after irradiation with a Solar Light Company model 16S solar simulator (equipped with a WG 320 filter to transmit radiation greater than 290 nm) in 5 MED increments up to 35 MED. Output was monitored by a PMA 2105 UV-B DCS Detector (biologically weighted) and controlled by a PMA 2100 Automatic Dose Controller (Solar Light Co.). After the composition had been exposed to 35 MED of irradiation, the absorbance of each composition was measured between 280 nm and 400 nm (the UV-B range). The resulting absorbance spectra are shown in Figure 12. The formulation of Table X was also tested, in the same manner, using UV-A radiation (320 nm to 400 nm). The resulting absorbance spectra are shown in Figure 13.

In addition to the level of absorbance for each composition in the UV-A and UV-B range, the absorption spectra also indicate the stability of each composition after irradiation at 35 MED. The stability of the composition can be measured against the negative control composition containing no CP and no oxybenzone and to the composition (O MED) which was not exposed to any irradiation. Figures 12 and 13 show an increase in the photostability with the addition of 4% by weight of hexanedioic acid, polymer with 2-methyl-2,3-propanediol, bis(2-cyano-3,3-diphenyl-2-propenoate) (CP) to a composition including 4% by weight of oxybenzone, in both the UV-A and UV-B ranges.

Surprisingly, the combination of 4% oxybenzone and 4% CP is equivalent to the O MED composition, which was not subjected to irradiation, after exposure to both UV-A and UV-B radiation.

Amounts of copolymer (CP) as low as 0.1%, preferably at least 0.2%, are sufficient to form a synergistic combination with oxybenzone, to photostabilize a sunscreen composition containing a UV-absorbent sunscreen compound, particularly a dibenzoylmethane derivative, such as avobenzone. The amount of the copolymer (CP)

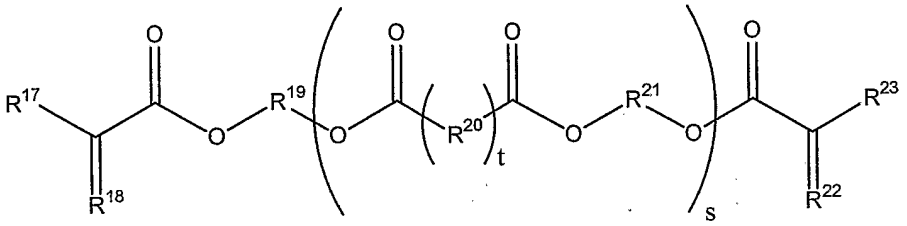
should be in the range of about 0.1% to about 15% by weight of the sunscreen formulation, preferably about 0.2% to about 10% by weight, more preferably about 0.3% to about 5% by weight of the sunscreen formulation. The amount of oxybenzone should be in the range of about 0.5% to about 15% by weight of the sunscreen formulation, preferably about 1% to about 10% by weight, more preferably about 4% to about 8% by weight of the sunscreen formulation.

As shown in the data of Table X and in the graphs of Figures 12 and 13, the copolymer (CP) and oxybenzone act synergistically to photostabilize avobenzone. The amount of CP should be at least 2.5% by weight based on the weight of oxybenzone, *e.g.*, at least 0.1% CP in a formulation containing 4.0% by weight oxybenzone. The weight ratio of the copolymer (CP) to the oxybenzone should be in the range of about 0.025 to about 5.0, preferably about 0.03 to 1.5, more preferably about 0.05 to 1.0, even more preferably about 0.1 to about 0.75.

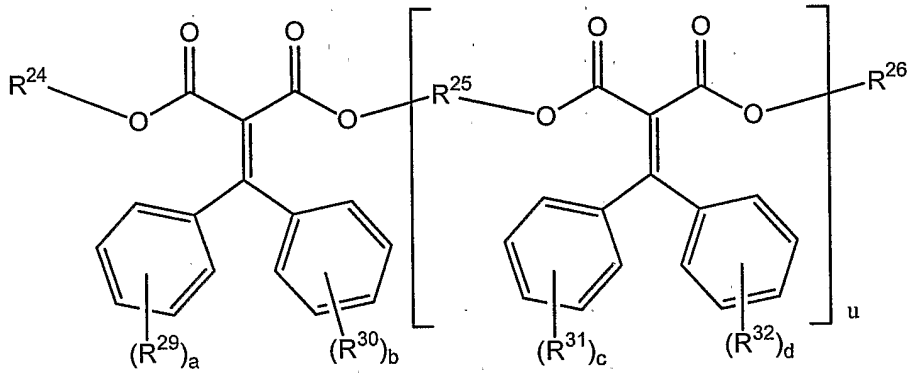
The foregoing description is given for clearness of understanding only, and no unnecessary limitations should be understood therefrom, as modifications within the scope of the invention may be apparent to those having ordinary skill in the art.

WHAT IS CLAIMED IS:

1. A sunscreen composition, comprising a mixture of a photoactive compound and a compound selected from the group consisting of compounds of formula (IX), compounds of formula (X), and combinations thereof:



(IX)



(X)

wherein, R^{19}, R^{20}, R^{21}, R^{24}, R^{25}, R^{26}, R^{29}, R^{30}, R^{31}, and R^{32} are the same or different and are selected from the group consisting of C_1-C_{30} alkyl, C_3-C_8 cycloalkyl, substituted alkyl, substituted cycloalkyl, ester, aryl, heteroaryl, heterocycloalkyl, substituted aryl, substituted heteroaryl, substituted heterocycloalkyl, and amino; R^{17} and R^{23} are the same or different and are selected from the group consisting of C_1-C_{30} alkyl, C_3-C_8 cycloalkyl, substituted alkyl, substituted cycloalkyl, ester, aryl, heteroaryl, heterocycloalkyl, substituted aryl, substituted heteroaryl, substituted heterocycloalkyl, cyano, and amino; R^{18} and R^{22} are the same or different and are selected from the group consisting of substituted diphenylmethylene, unsubstituted diphenylmethylene, substituted 9*H*-fluorene, and unsubstituted 9*H*-fluorene; t and u are each in the range of 1 to 100; s is in the range of 0 to 100; and a, b, c, and d are each in the range of 0 to 4.

2. The composition of claim 1, wherein R^{19}, R^{20} and R^{21} are selected from the group consisting of C_1-C_{15} branched chain alkyls.

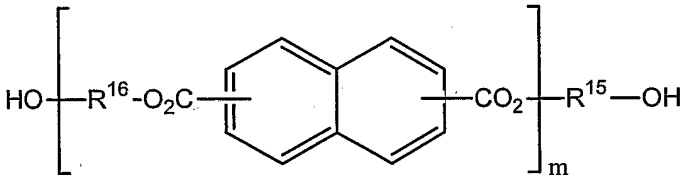
3. The composition of claim 1, wherein R^{17} and R^{23} are the same and are cyano.

4. The composition of claim 1, wherein said compound of formula (IX) is present in a range of about 0.1% to about 25% by weight of the total weight of the composition.

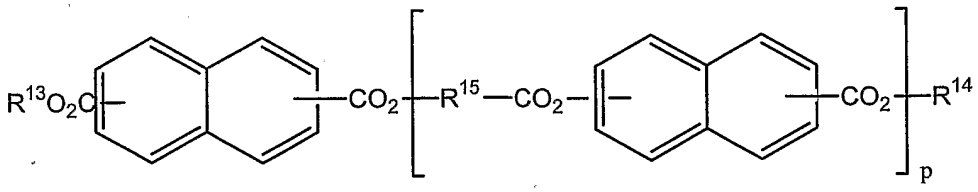
5. The composition of claim 4 wherein said compound of formula (IX) is present in a range of about 0.1% to about 10% by weight of the total weight of the composition.

6. The composition of claim 1, comprising a dibenzoylmethane derivative.

7. The composition of claim 1, further comprising a diester or polyester of naphthalene dicarboxylic acid selected from the group consisting of compounds of formula (VII), formula (VIII), and combinations thereof:



(VII)

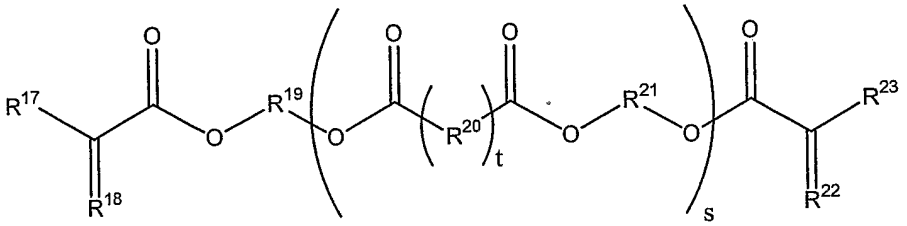


(VIII)

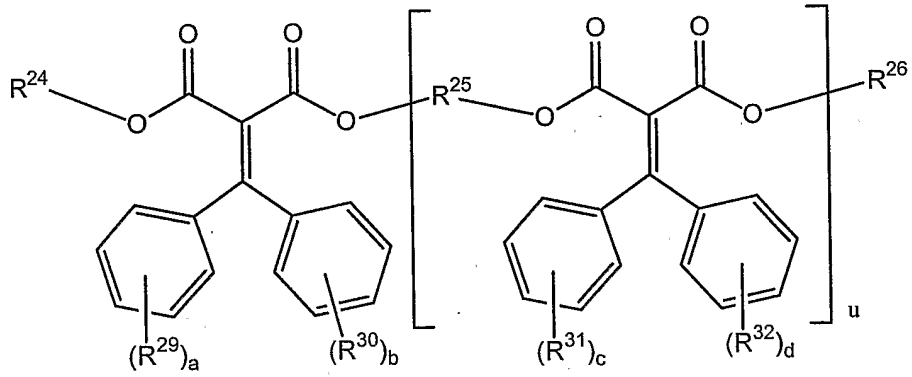
wherein R^{13} and R^{14} are the same or different and selected from the group consisting of C_1-C_{22} alkyl groups, diols having the structure HO—R^{15}—OH, and polyglycols having the structure HO—R^{16}—(—O—R^{15}—)$_n$—OH; wherein each R^{15} and R^{16} is the same or different and selected from the group consisting of C_1-C_6 straight or branched chain alkyl groups; and wherein m and n are each in a range of 1 to 100 and p is in a range of 0 to 100.

8. A sunscreen composition, comprising a mixture of a photoactive compound; about 0.1% to about 15% by weight of a compound selected from the group

consisting of compounds of formula (IX), compounds of formula (X), and combinations thereof:

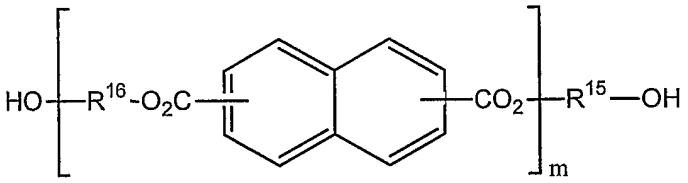


(IX)

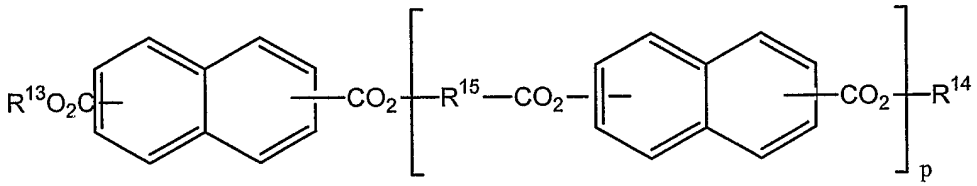


(X)

wherein, R^{19}, R^{20}, R^{21}, R^{24}, R^{25}, R^{26}, R^{29}, R^{30}, R^{31}, and R^{32} are the same or different and are selected from the group consisting of C_1-C_{30} alkyl, C_3-C_8 cycloalkyl, substituted alkyl, substituted cycloalkyl, ester, aryl, heteroaryl, heterocycloalkyl, substituted aryl, substituted heteroaryl, substituted heterocycloalkyl, and amino; R^{17} and R^{23} are the same or different and are selected from the group consisting of C_1-C_{30} alkyl, C_3-C_8 cycloalkyl, substituted alkyl, substituted cycloalkyl, ester, aryl, heteroaryl, heterocycloalkyl, substituted aryl, substituted heteroaryl, substituted heterocycloalkyl, cyano, and amino; R^{18} and R^{22} are the same or different and are selected from the group consisting of substituted diphenylmethylene, unsubstituted diphenylmethylene, substituted 9*H*-fluorene, and unsubstituted 9*H*-fluorene; t and u are each in the range of 1 to 100; s is in the range of 0 to 100; and a, b, c, and d are each in the range of 0 to 4; and about 2% to about 15% by weight of a diester or polyester of naphthalene dicarboxylic acid selected from the group consisting of compounds of formula (VII), formula (VIII), and combinations thereof:



(VII)



(VIII)

wherein R^{13} and R^{14} are the same or different and selected from the group consisting of C_1-C_{22} alkyl groups, diols having the structure HO—R^{15}—OH, and polyglycols having the structure HO—R^{16}—(—O—R^{15}—)$_n$—OH; wherein each R^{15} and R^{16} is the same or different and selected from the group consisting of C_1-C_6 straight or branched chain alkyl groups; and wherein m and n are each in a range of 1 to 100 and p is in a range of 0 to 100.

9. The composition of claim 8, wherein R^{19}, R^{20} and R^{21} are selected from the group consisting of C_1-C_{15} branched chain alkyls.

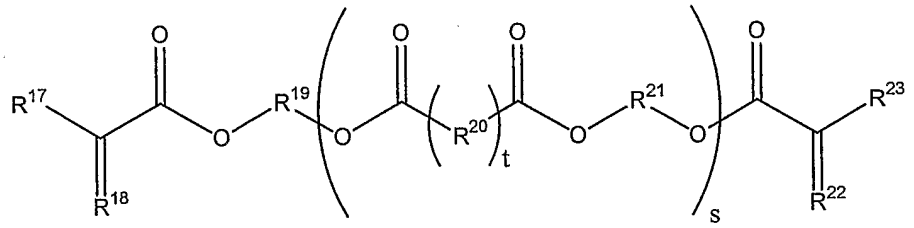
10. The composition of claim 8, wherein R^{17} and R^{23} are the same and are cyano and R^{18} and R^{22} are the same and are diphenylmethylene.

11. The composition of claim 8, wherein the composition includes one or more compounds of formula (IX) or (X) or a combination of (IX) and (X) in a weight ratio to one or more compounds of formula (VII) or (VIII) or a combination of (VII) and (VIII) in the range of 0.02 to 5.0.

12. The composition of claim 11, wherein said weight ratio is in the range of 0.02 to 1.5.

13. The composition of claim 8, comprising a diester of formula (VIII) wherein R^1 and R^2 are 2-ethylhexane and p is 0.

14. A compound of formula (IX),



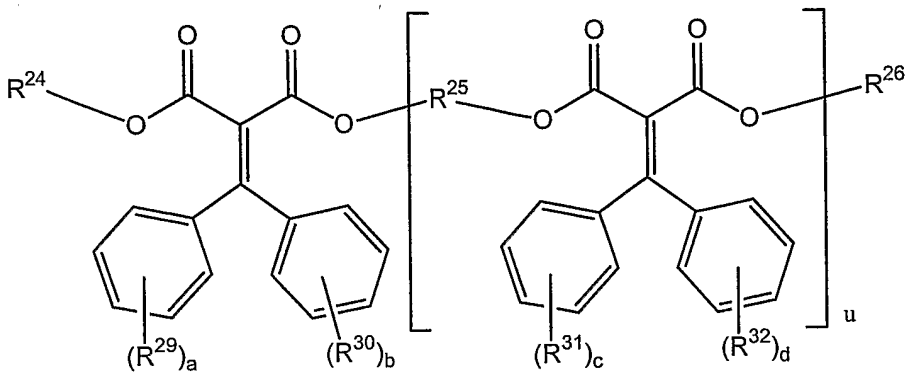
(IX)

wherein, R^{19}, R^{20}, and R^{21} are the same or different and are selected from the group consisting of C_1-C_{30} alkyl, C_3-C_8 cycloalkyl, substituted alkyl, substituted cycloalkyl, ester, aryl, heteroaryl, heterocycloalkyl, substituted aryl, substituted heteroaryl, substituted heterocycloalkyl, and amino; R^{17} and R^{23} are the same or different and are selected from the group consisting of C_1-C_{30} alkyl, C_3-C_8 cycloalkyl, substituted alkyl, substituted cycloalkyl, ester, aryl, heteroaryl, heterocycloalkyl, substituted aryl, substituted heteroaryl, substituted heterocycloalkyl, cyano, and amino; R^{18} and R^{22} are the same or different and are selected from the group consisting of substituted diphenylmethylene, unsubstituted diphenylmethylene, substituted 9*H*-fluorene, and unsubstituted 9*H*-fluorene; t is in the range of 1 to 100; and s is in the range of 0 to 100.

15. The compound of claim 14, wherein R^{19}, R^{20} and R^{21} are selected from the group consisting of C_1-C_{15} branched chain alkyls.

16. The compound of claim 14, wherein R^{17} and R^{23} are the same and are cyano.

17. A compound of formula (X):



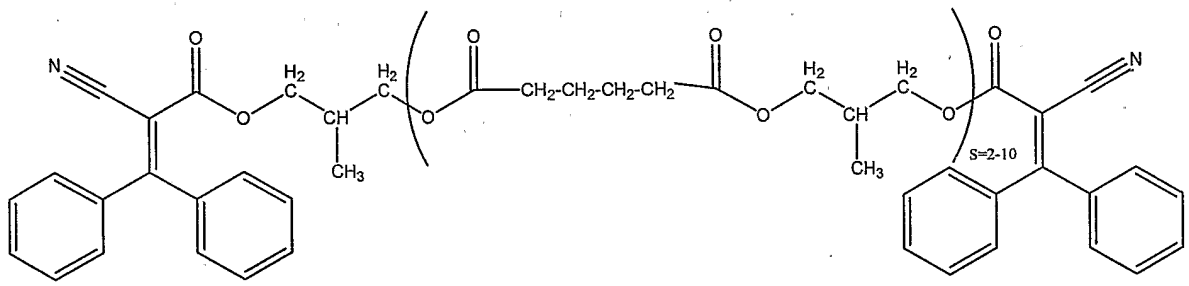
(X)

wherein R^{24}, R^{25}, R^{26}, R^{29}, R^{30}, R^{31}, and R^{32} are the same or different and are selected from the group consisting of C_1-C_{30} alkyl, C_3-C_8 cycloalkyl, substituted alkyl, substituted cycloalkyl, ester, aryl, heteroaryl, heterocycloalkyl, substituted aryl, substituted heteroaryl, substituted heterocycloalkyl, and amino; u is in the range of 1 to 100; and a, b, c, and d are each in the range of 0 to 4.

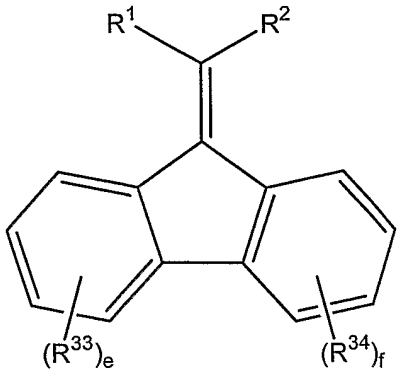
18. The compound of claim 17, wherein R^{24}, R^{25}, and R^{26} are selected from the group consisting of C_3-C_{15} branched chain alkyl groups.

19. The compound of claim 18, wherein R^{24} and R^{26} are 2-ethylhexane.

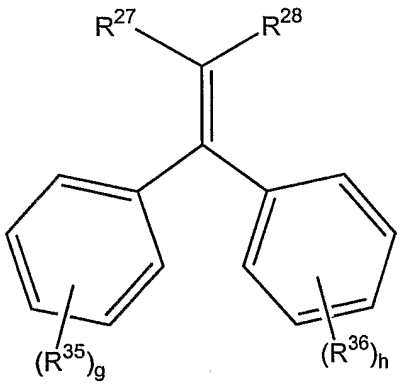
20. A compound having the following structure:



21. A method of making a polymer, comprising terminating a polymer chain with a compound selected from the group consisting of compounds of formula (XII), compounds of formula (XI), and combinations thereof:



(XII)



(XI)

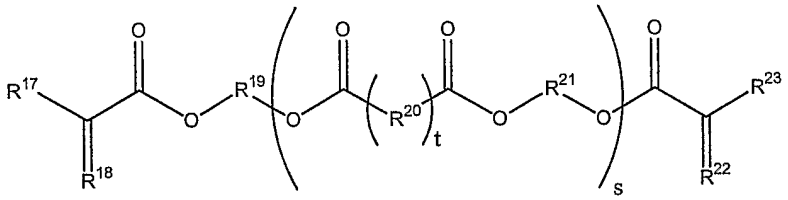
wherein R^1 and R^{27} are cyano; R^2, R^{28}, R^{33}, R^{34}, R^{35}, and R^{36} are the same or different and are selected from the group consisting of C_1-C_{30} alkyl, C_3-C_8 cycloalkyl, substituted alkyl, substituted cycloalkyl, ester, aryl, heteroaryl, heterocycloalkyl, substituted aryl, substituted heteroaryl, substituted heterocycloalkyl, cyano, and amino; and e, f, g, h are each in the range of 0 to 4.

22. The method of claim 21, wherein said polymer chain is selected from the group consisting of polyesters, polyamides, polyolefins, polyurethanes, and combinations thereof.

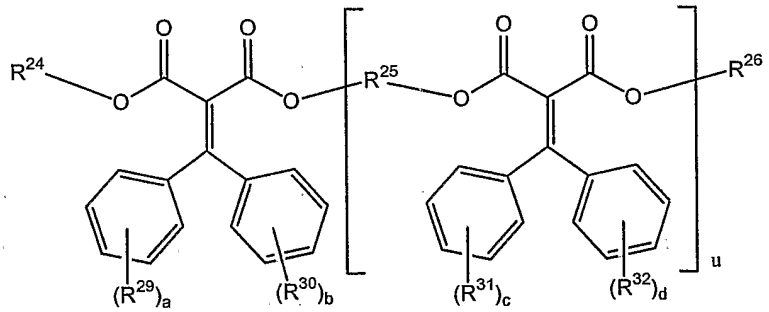
23. A method of protecting human skin from ultraviolet radiation comprising topically applying to said skin, in a cosmetically acceptable carrier, the composition of claim 8.

24. The method of claim 23, wherein R^{17} and R^{23} are the same and are cyano; R^{18} and R^{22} are the same and are diphenylmethylene; R^{20} is C_4H_8; t = 1; R^{19} and R^{21} are C_3H_9; and s = 1-5.

25. A method of protecting human skin from ultraviolet radiation comprising topically applying to said skin, in a cosmetically acceptable carrier, a compound selected from the group consisting of compounds of formula (IX), compounds of formula (X), and combinations thereof:



(IX)



(X)

wherein, R^{19}, R^{20}, R^{21}, R^{24}, R^{25}, R^{26}, R^{29}, R^{30}, R^{31}, and R^{32} are the same or different and are selected from the group consisting of C_1-C_{30} alkyl, C_3-C_8 cycloalkyl, substituted alkyl, substituted cycloalkyl, ester, aryl, heteroaryl, heterocycloalkyl, substituted aryl, substituted heteroaryl, substituted heterocycloalkyl, and amino; R^{17} and R^{23} are the same or different and are selected from the group consisting of C_1-C_{30} alkyl, C_3-C_8 cycloalkyl, substituted alkyl, substituted cycloalkyl, ester, aryl, heteroaryl, heterocycloalkyl, substituted aryl, substituted heteroaryl, substituted heterocycloalkyl, cyano, and amino; R^{18} and R^{22} are the same or different and are selected from the group consisting of substituted diphenylmethylene, unsubstituted diphenylmethylene, substituted 9*H*-fluorene, and unsubstituted 9*H*-fluorene; t and u are each in the range of 1 to 100; s is in the range of 0 to 100; and a, b, c, and d are each in the range of 0 to 4.

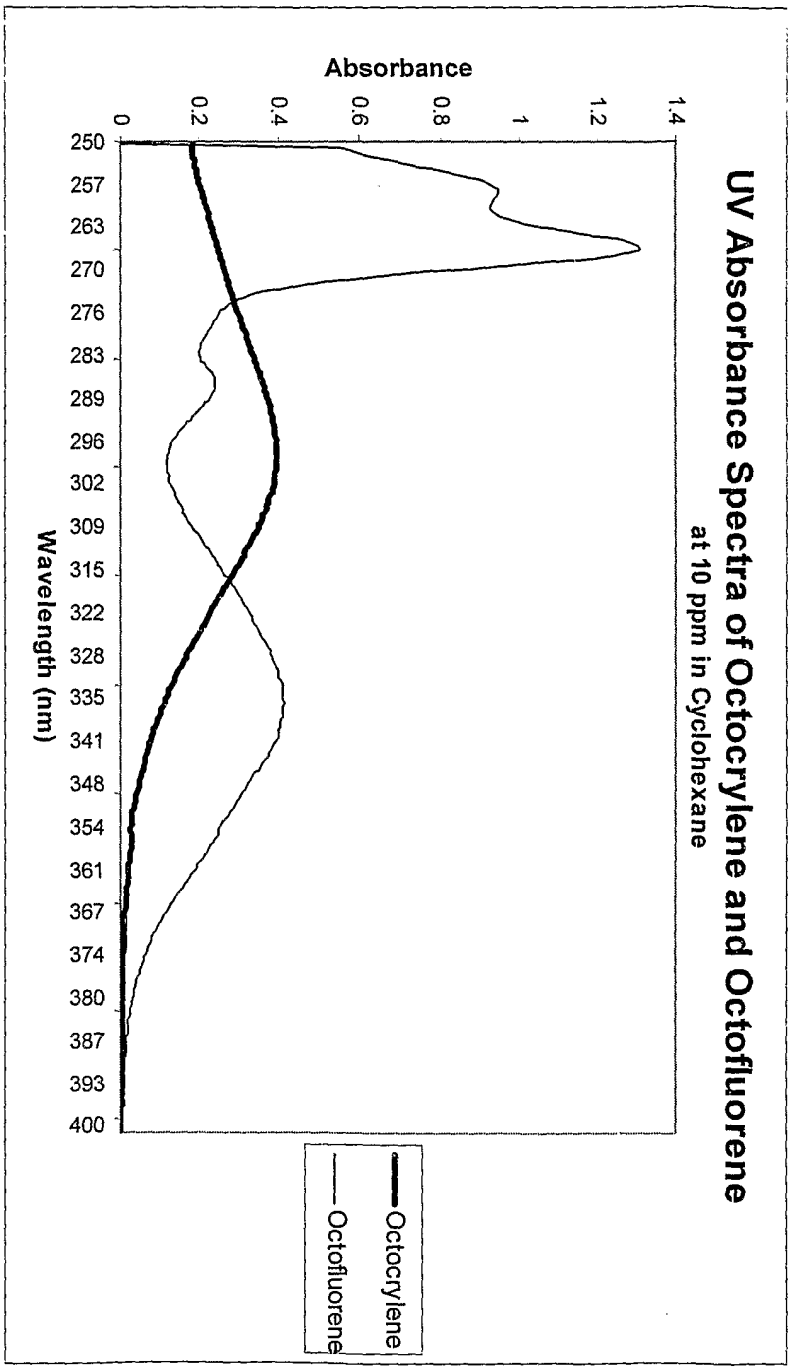

UV Absorbance Spectra of Octocrylene and Octofluorene
at 10 ppm in Cyclohexane
Absorbance
0
0.2
0.4
0.6
0.8
1
1.2
1.4
Wavelength (nm)
250
257
263
270
276
283
289
296
302
309
315
322
328
335
341
348
354
361
367
374
380
387
393
400
Octocrylene
Octofluorene

FIGURE 1

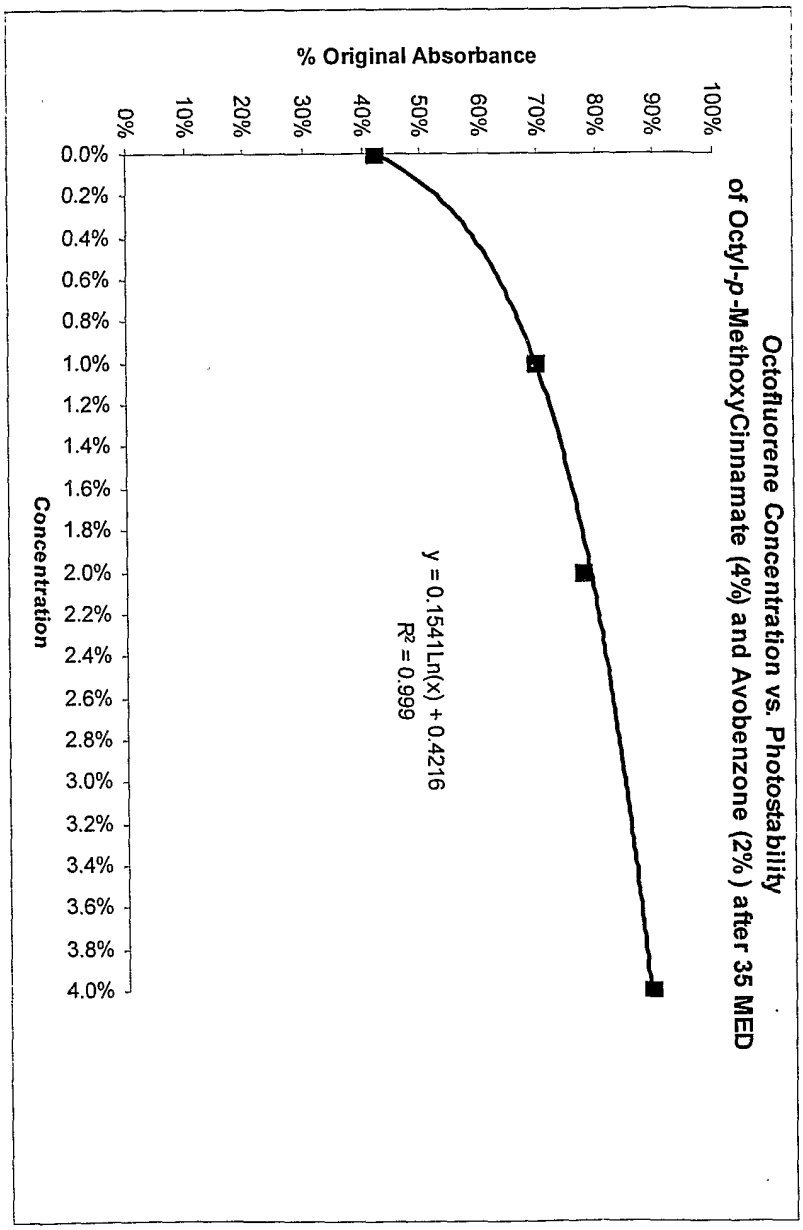

Octofluorene Concentration vs. Photostability
of Octyl-p-MethoxyCinnamate (4%) and Avobenzone (2%) after 35 MED
% Original Absorbance
0%
10%
20%
30%
40%
50%
60%
70%
80%
90%
100%
Concentration
0.0%
0.2%
0.4%
0.6%
0.8%
1.0%
1.2%
1.4%
1.6%
1.8%
2.0%
2.2%
2.4%
2.6%
2.8%
3.0%
3.2%
3.4%
3.6%
3.8%
4.0%
y = 0.1541Ln(x) + 0.4216
R² = 0.999

FIGURE 2

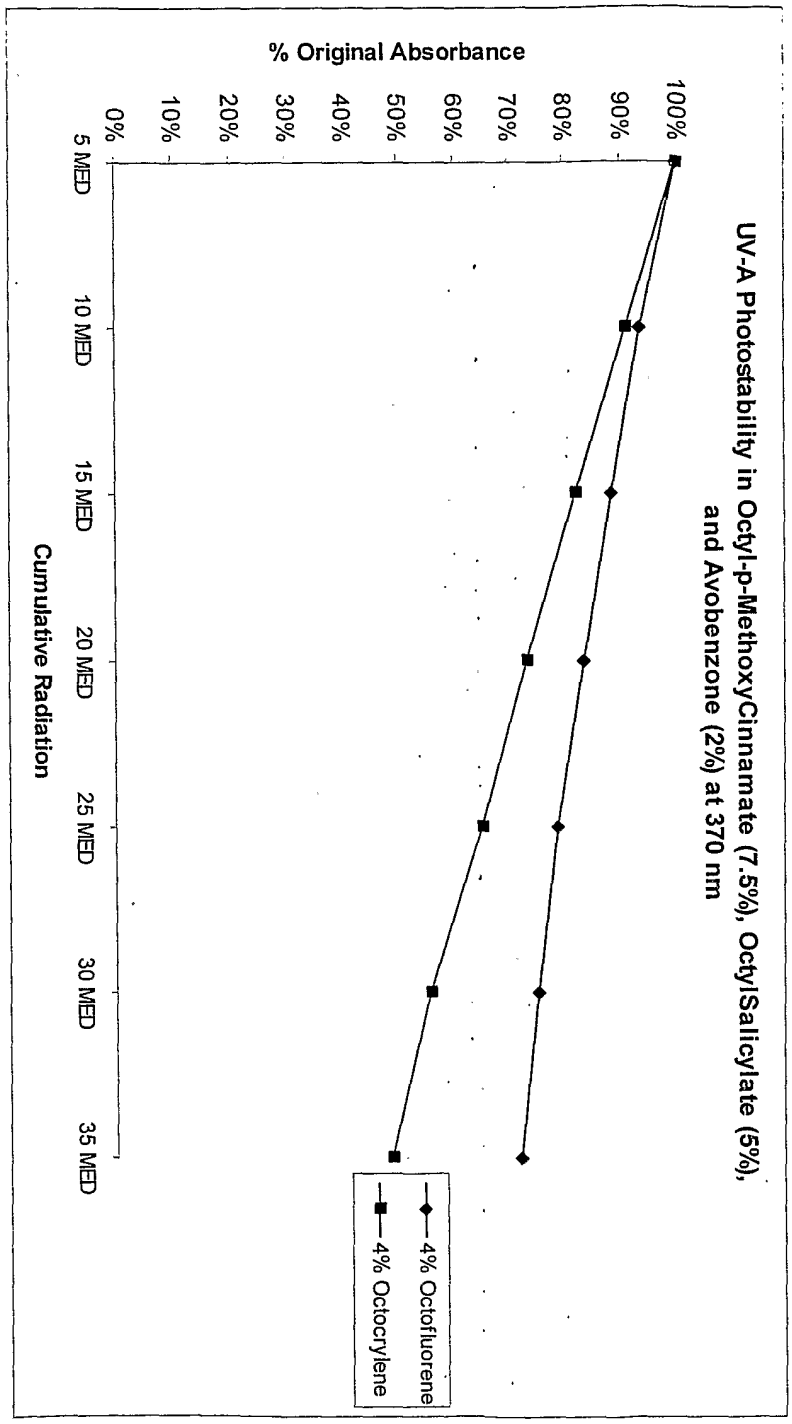

UV-A Photostability in Octyl-p-MethoxyCinnamate (7.5%), OctylSalicylate (5%), and Avobenzone (2%) at 370 nm
% Original Absorbance
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
5 MED
10 MED
15 MED
20 MED
25 MED
30 MED
35 MED
Cumulative Radiation
4% Octofluorene
4% Octocrylene

FIGURE 3

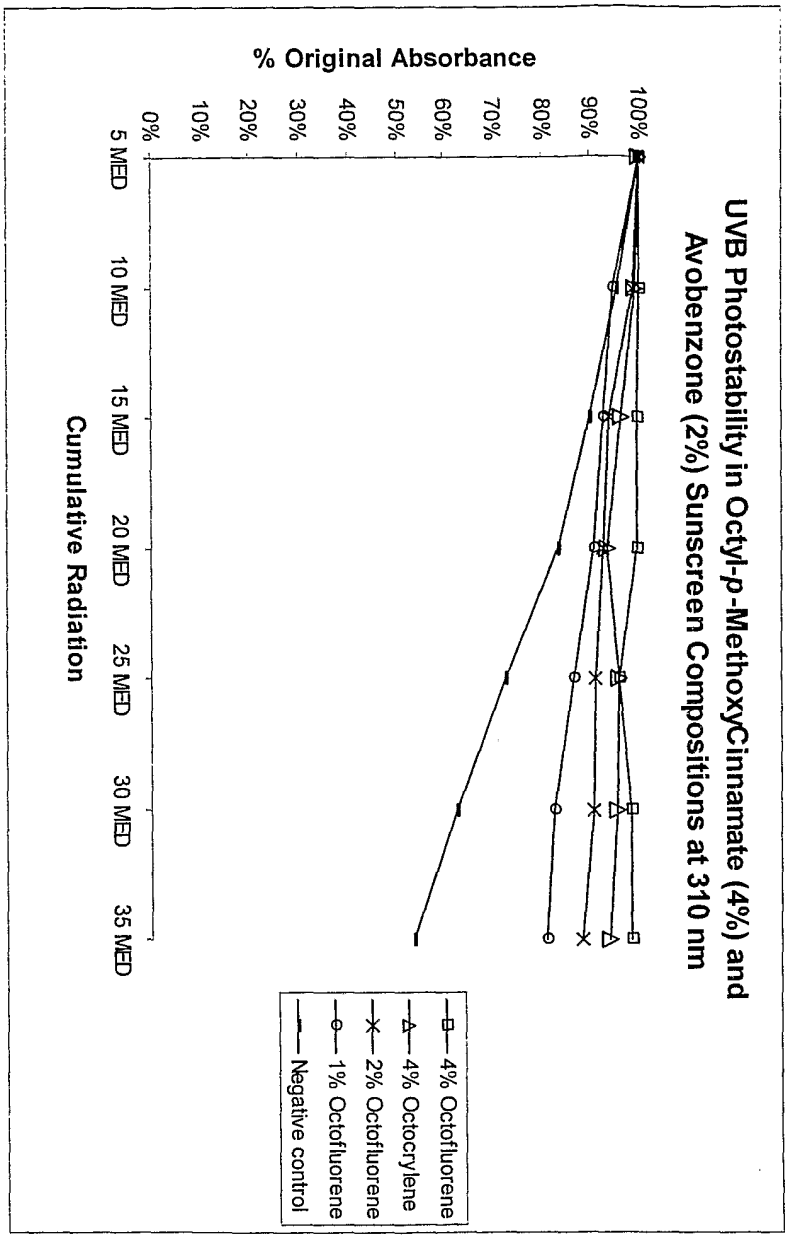

UVB Photostability in Octyl-p-MethoxyCinnamate (4%) and Avobenzone (2%) Sunscreen Compositions at 310 nm
% Original Absorbance
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
5 MED
10 MED
15 MED
20 MED
25 MED
30 MED
35 MED
Cumulative Radiation
4% Octofluorene
4% Octocrylene
2% Octofluorene
1% Octofluorene
Negative control

FIGURE 4

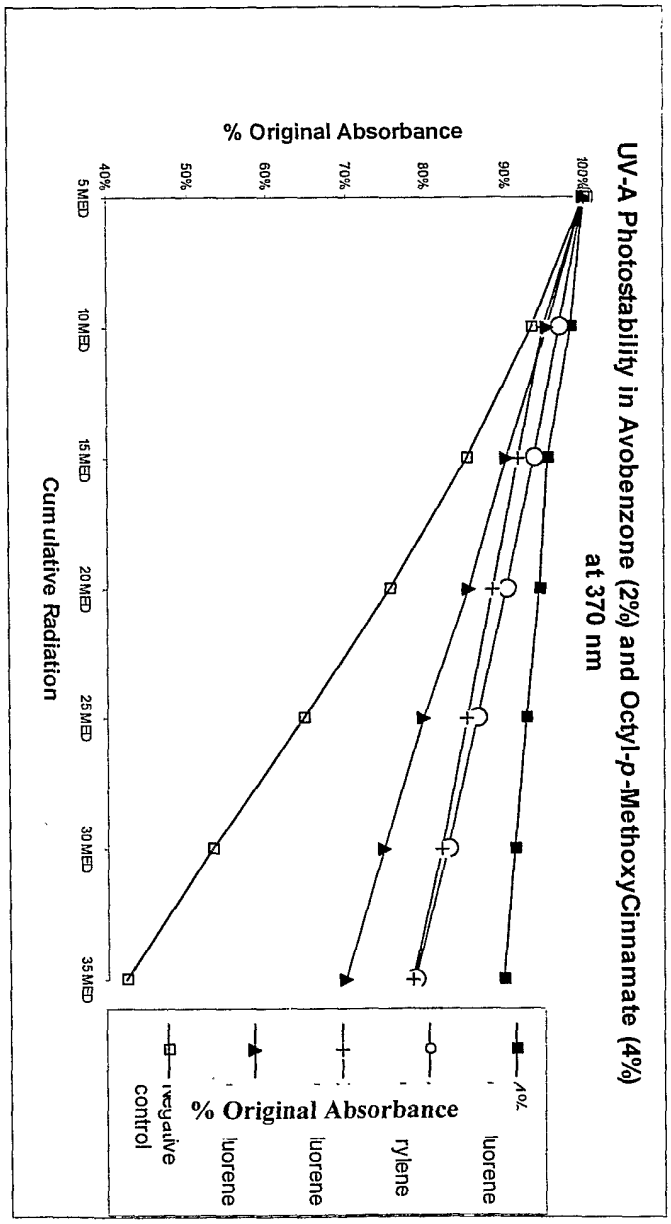

UV-A Photostability in Avobenzone (2%) and Octyl-p-MethoxyCinnamate (4%)
at 370 nm
% Original Absorbance
100%
90%
80%
70%
60%
50%
40%
5 MED
10 MED
15 MED
20 MED
25 MED
30 MED
35 MED
Cumulative Radiation
% Original Absorbance
4%
fluorene
rylene
fluorene
fluorene
negative control

FIGURE 5

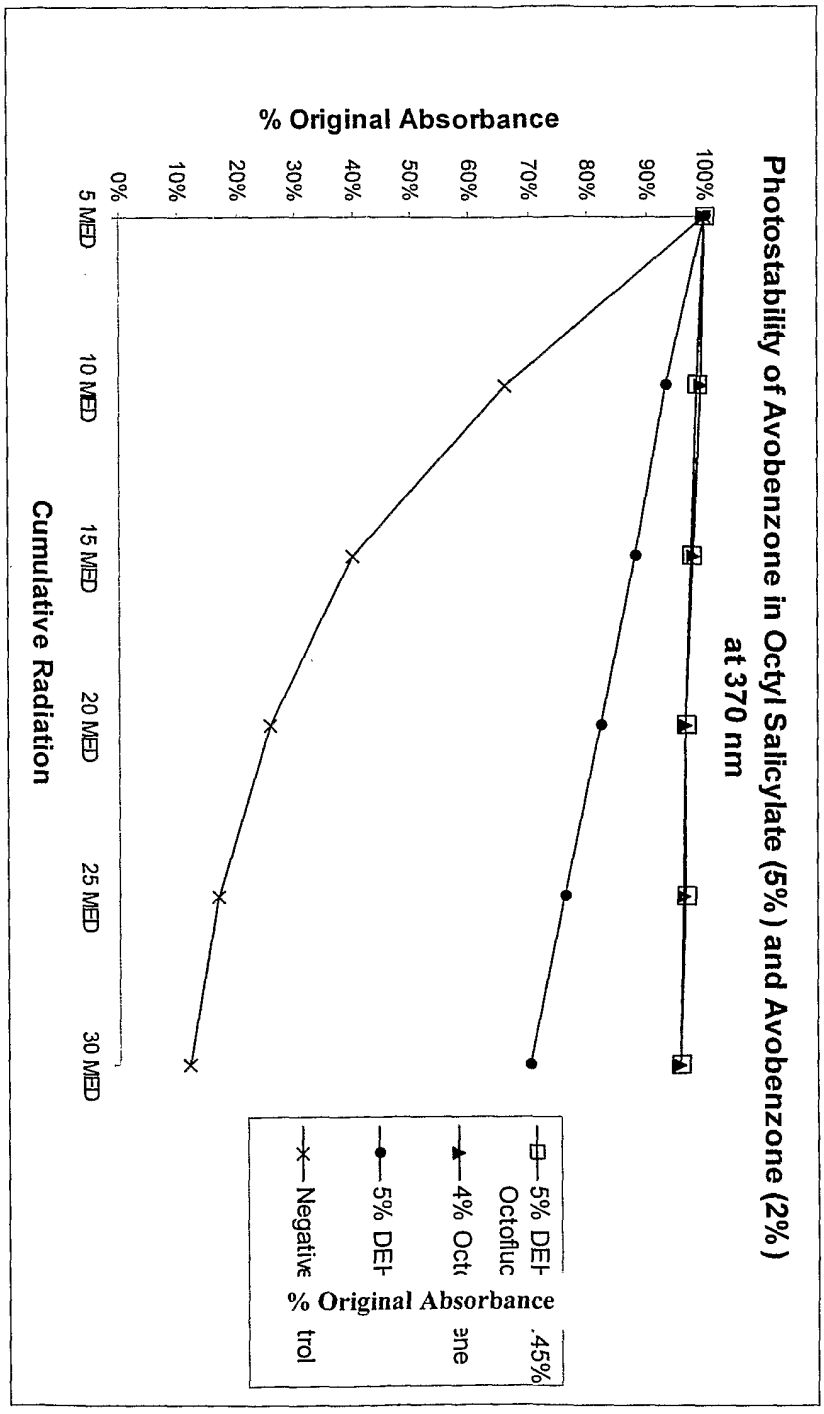

Photostability of Avobenzone in Octyl Salicylate (5%) and Avobenzone (2%)
at 370 nm
% Original Absorbance
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
5 MED
10 MED
15 MED
20 MED
25 MED
30 MED
Cumulative Radiation
5% DEH Octofluc .45%
4% Octe ene
5% DEH
Negative trol
% Original Absorbance

FIGURE 6

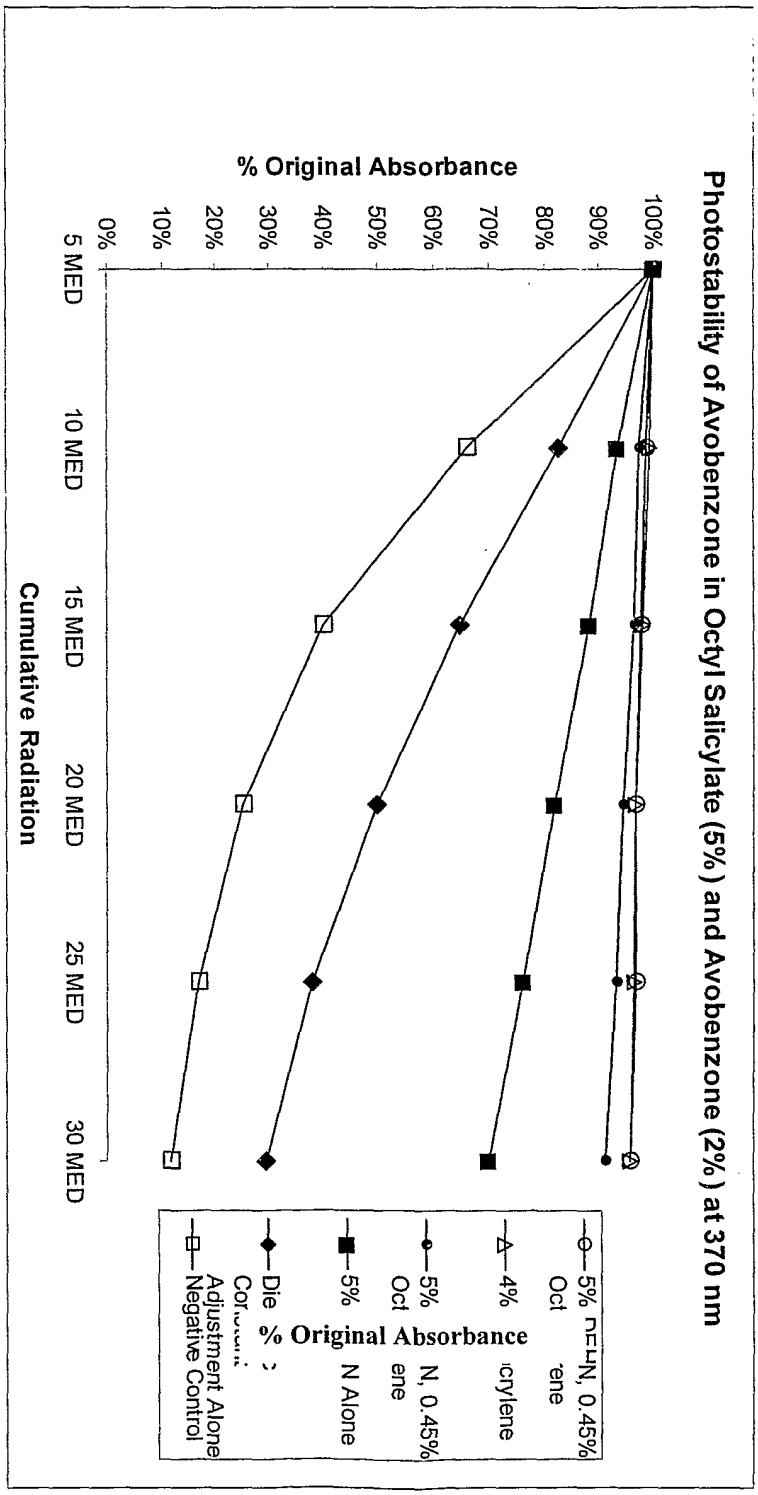

Photostability of Avobenzone in Octyl Salicylate (5%) and Avobenzone (2%) at 370 nm
% Original Absorbance
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
5 MED
10 MED
15 MED
20 MED
25 MED
30 MED
Cumulative Radiation
% Original Absorbance
5% Oct ene
4% crylene
5% Oct ene
5% N Alone
Die
Adjustment Alone
Negative Control

FIGURE 7

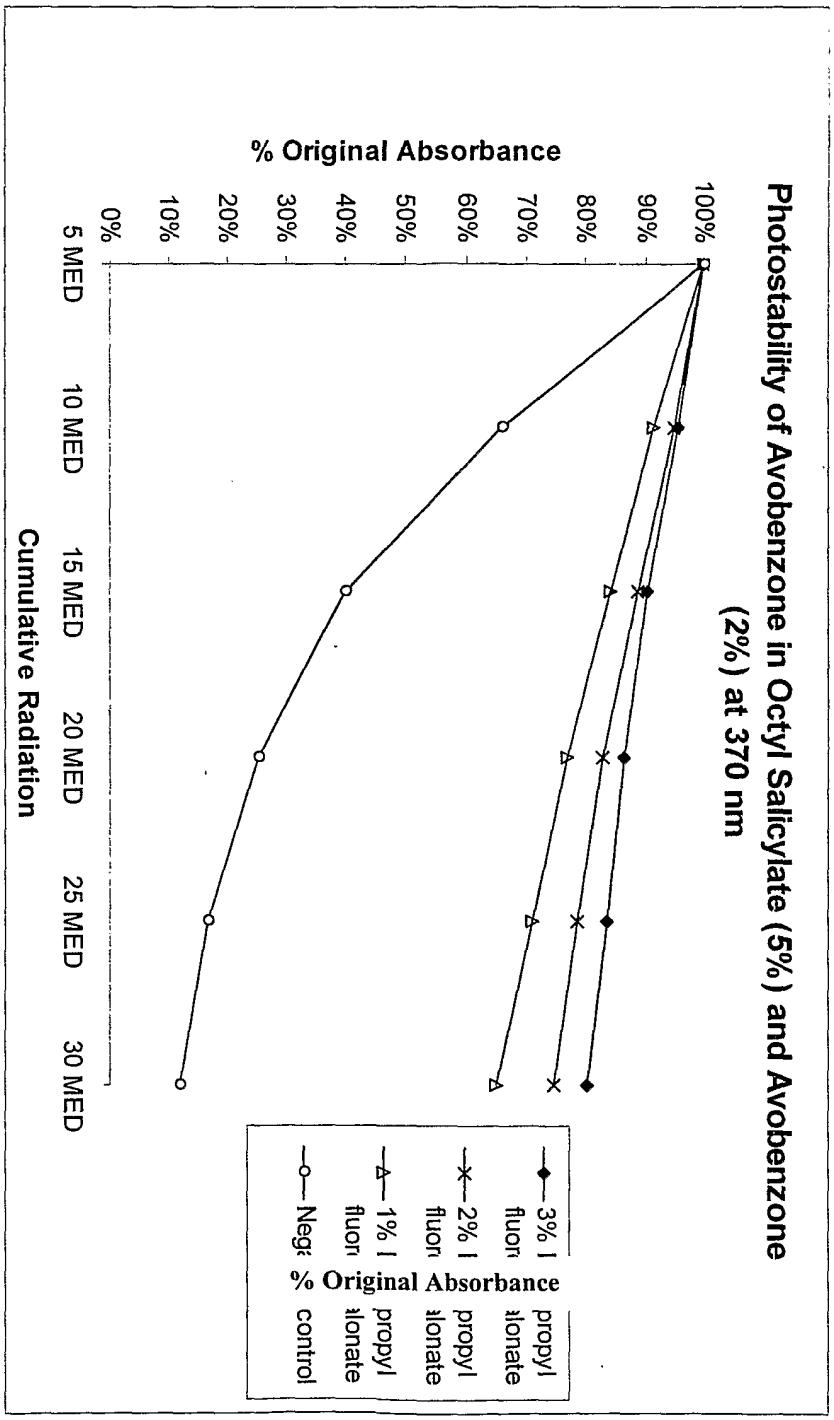

Photostability of Avobenzone in Octyl Salicylate (5%) and Avobenzone (2%) at 370 nm
% Original Absorbance
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
5 MED
10 MED
15 MED
20 MED
25 MED
30 MED
Cumulative Radiation
% Original Absorbance
3% l
fluon
propyl
alonate
2% l
fluon
propyl
alonate
1% l
fluon
propyl
alonate
Negs
control

FIGURE 8

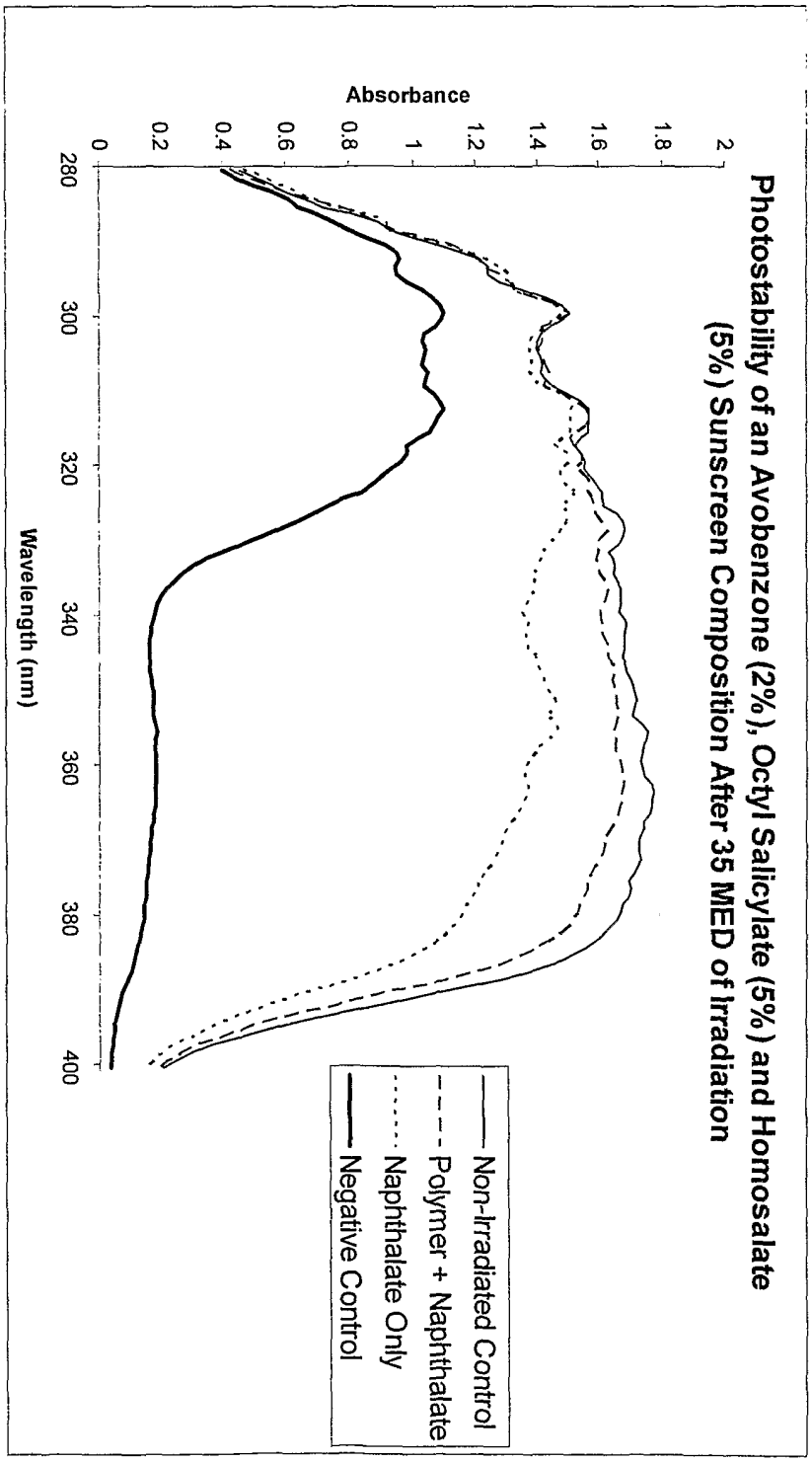

Photostability of an Avobenzone (2%), Octyl Salicylate (5%) and Homosalate (5%) Sunscreen Composition After 35 MED of Irradiation
Absorbance
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
Wavelength (nm)
280
300
320
340
360
380
400
Non-Irradiated Control
Polymer + Naphthalate
Naphthalate Only
Negative Control

FIGURE 9

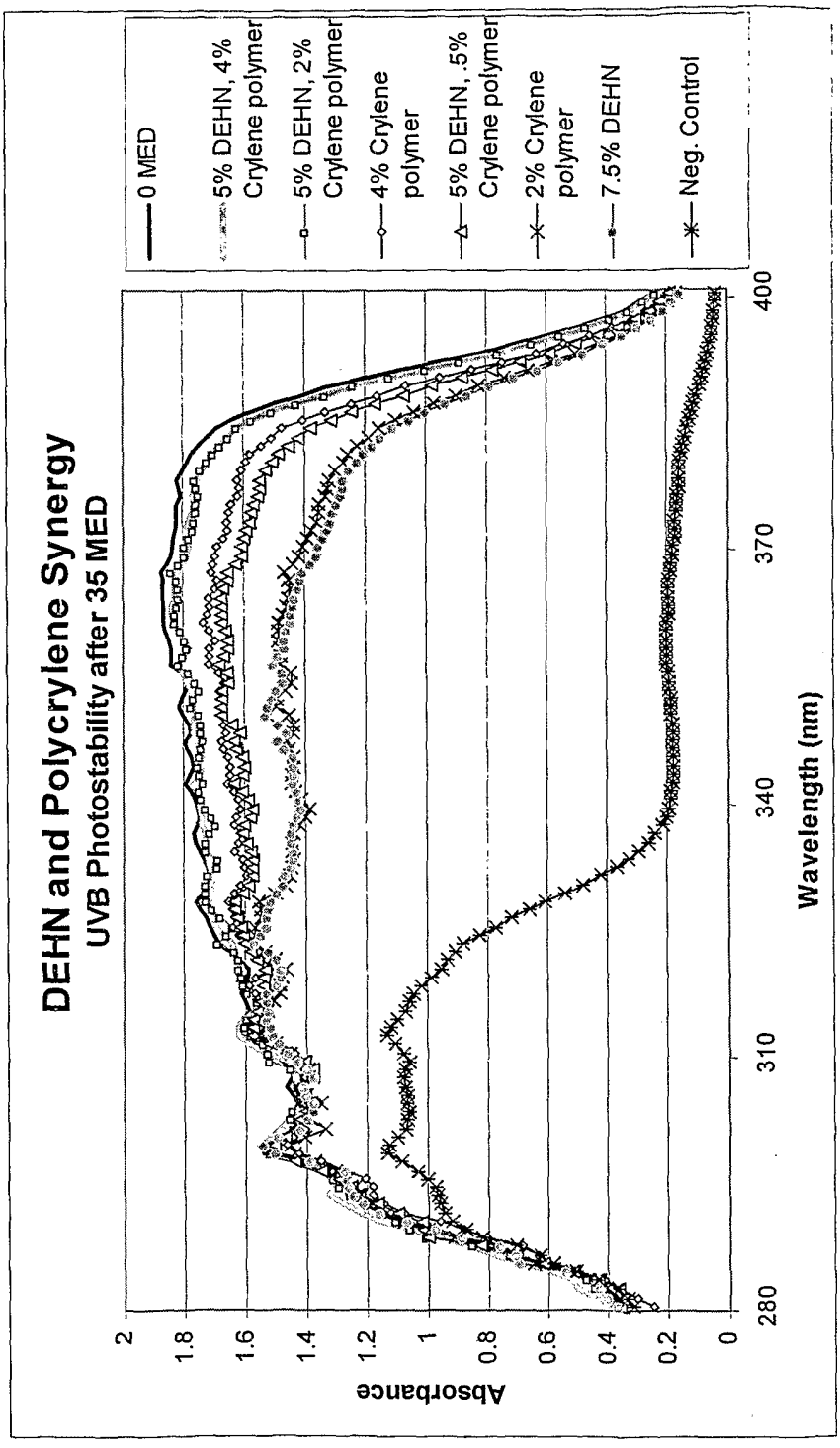

DEHN and Polycrylene Synergy
UVB Photostability after 35 MED
0 MED
5% DEHN, 4% Crylene polymer
5% DEHN, 2% Crylene polymer
4% Crylene polymer
5% DEHN, .5% Crylene polymer
2% Crylene polymer
7.5% DEHN
Neg. Control
Absorbance
Wavelength (nm)
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
280
310
340
370
400

FIGURE 10

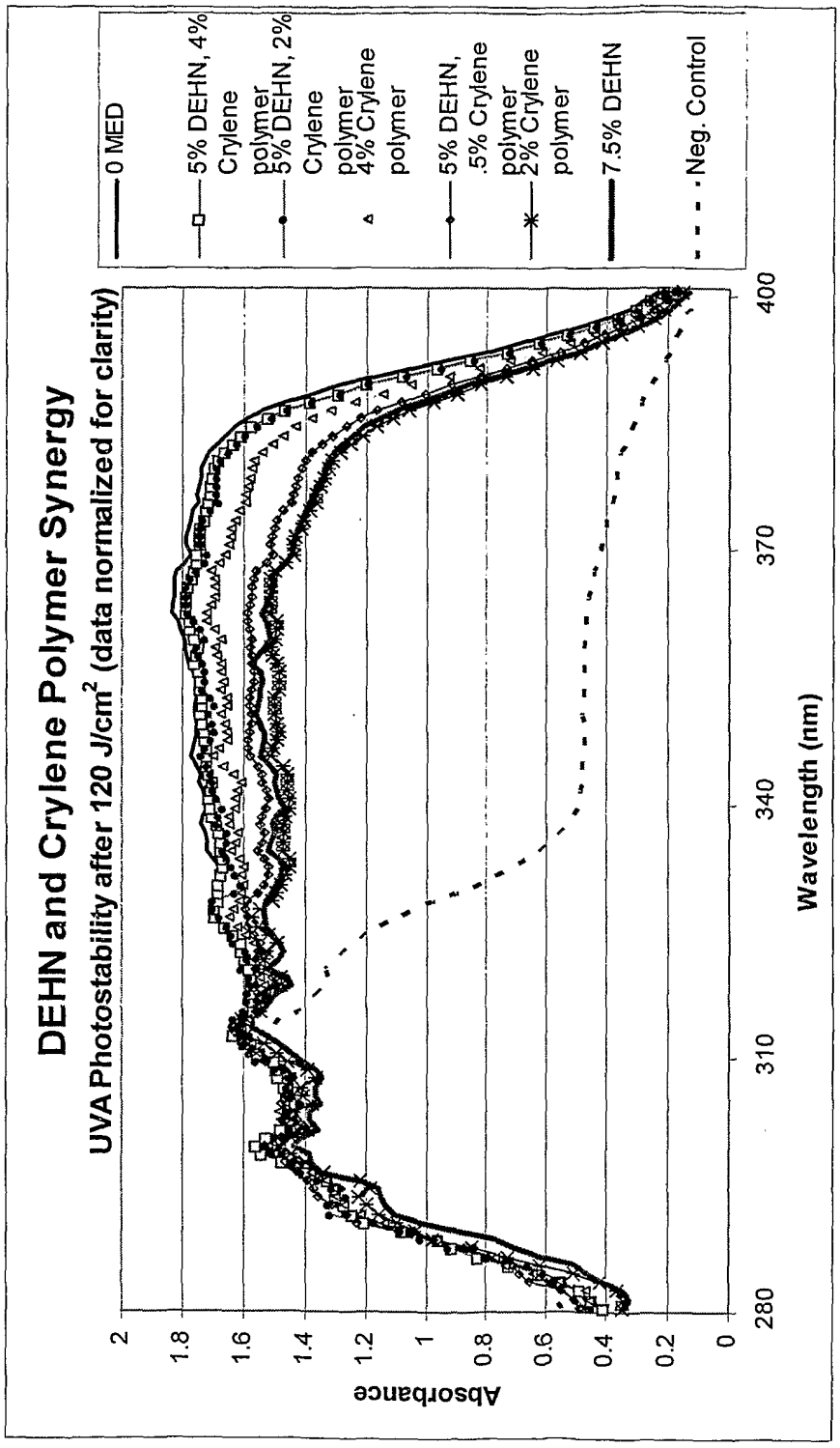

DEHN and Crylene Polymer Synergy
UVA Photostability after 120 J/cm2 (data normalized for clarity)
0 MED
5% DEHN, 4% Crylene polymer
5% DEHN, 2% Crylene polymer
4% Crylene polymer
5% DEHN, .5% Crylene polymer
2% Crylene polymer
7.5% DEHN
Neg. Control
Absorbance
Wavelength (nm)
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
280
310
340
370
400

FIGURE 11

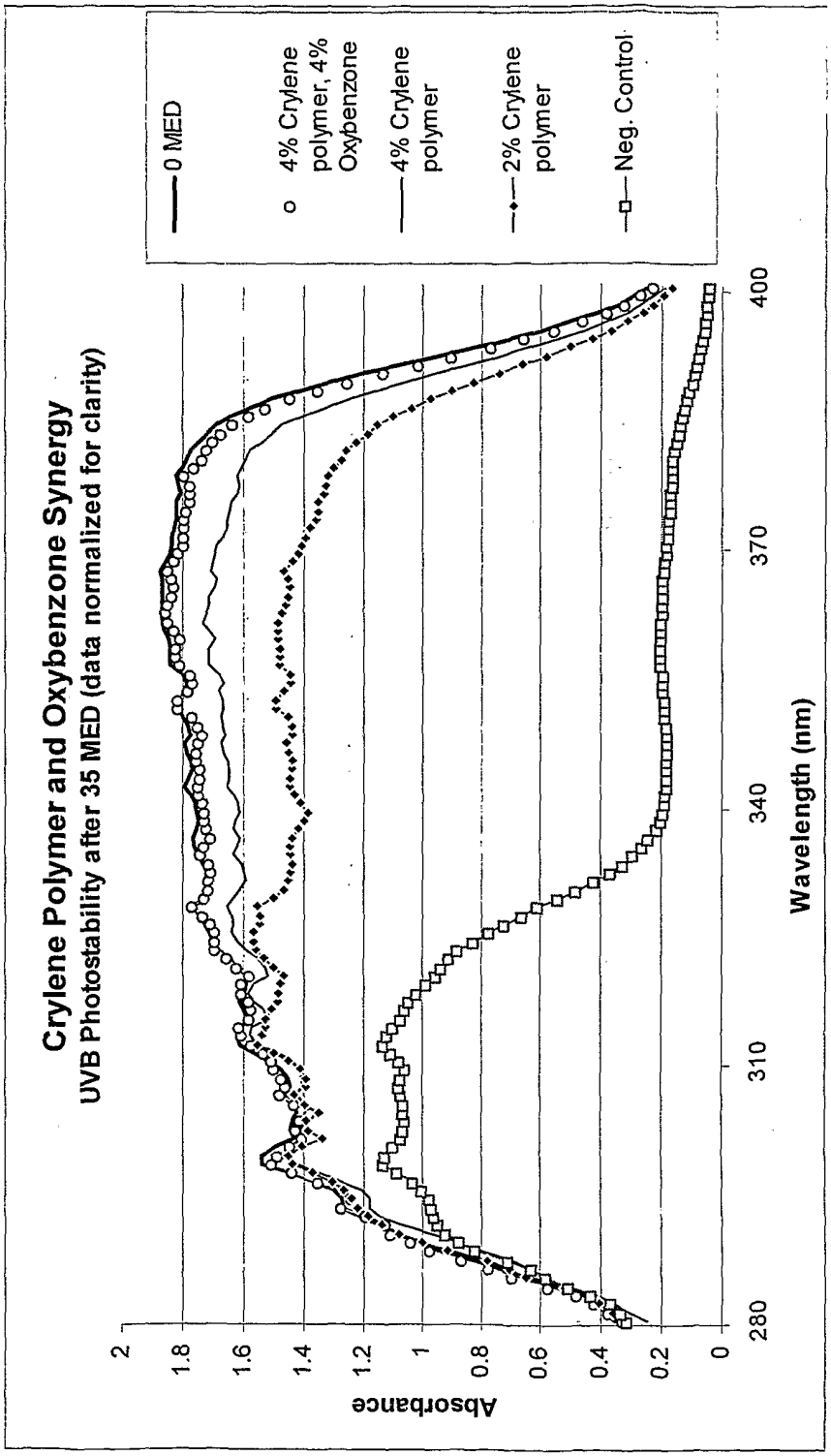

Crylene Polymer and Oxybenzone Synergy
UVB Photostability after 35 MED (data normalized for clarity)
0 MED
4% Crylene polymer, 4% Oxybenzone
4% Crylene polymer
2% Crylene polymer
Neg. Control
Absorbance
Wavelength (nm)
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
280
310
340
370
400

FIGURE 12

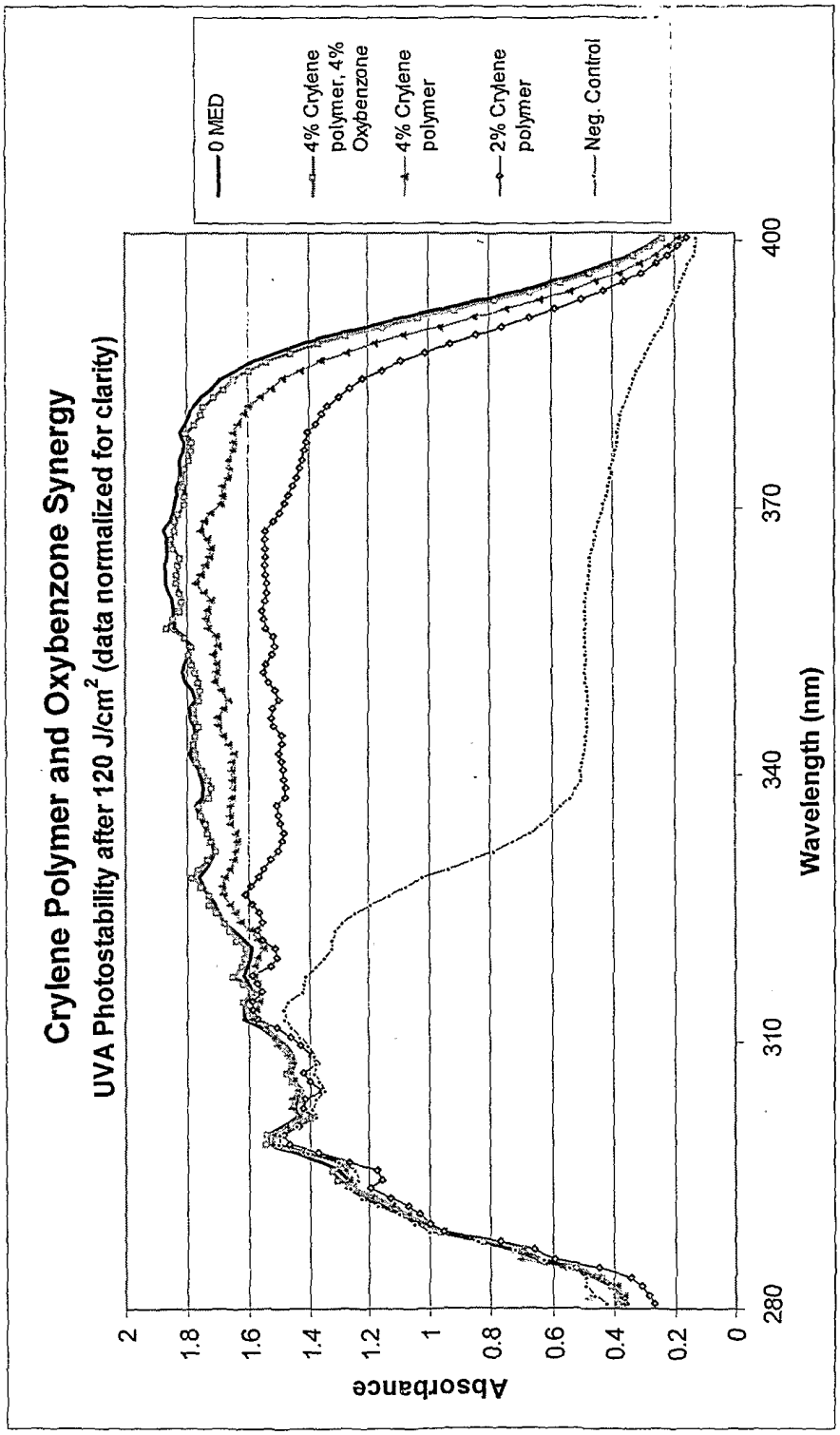

Crylene Polymer and Oxybenzone Synergy
UVA Photostability after 120 J/cm2 (data normalized for clarity)
0 MED
4% Crylene polymer, 4% Oxybenzone
4% Crylene polymer
2% Crylene polymer
Neg. Control
Absorbance
Wavelength (nm)
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
280
310
340
370
400

FIGURE 13